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AN INVESTIGATION OF METHODS FOR PREPARING SUBSTITUTED o- AND m-TERPHENYLS

A THESIS

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AN INVESTIGATION OF METHODS FOR PREPARING

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In addition, he wishes to thank Dr. Jack Hine and Dr. James Knight for their participation on his reading committee.

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SUMMARY

The object of this research was to investigate methods of synthesizing certain o- and m-terphenyls. These terphenyls were to have bulky substituents in the ortho position of the terminal phenyl groups so that there would be restriction of rotation around the carbon-carbon single bonds connecting these groups to the central ring.

Three general approaches were investigated. The first approach was characterized by the use of the Ullmann reaction as the means of coupling bulky aromatic groups.

The initial attempt of this first approach was intended to culminate in the preparation of trimethyl 2,2"-dinitro-o-terphenyl-3',6,6"-tricarboxylate from the coupling of dimethyl 6-iodo-6'-nitrodiphenate with methyl 2-bromo-3-nitrobenzoate. However, unexpected side reactions obviated the preparation of dimethyl 6-iodo-6'-nitrodiphenate. The attempted synthesis of this iodo compound started with the preparation of dimethyl 6,6'-dinitrodiphenate which was then to be reduced selectively to dimethyl 6-amino-6'-nitrodiphenate. The selective reduction of dimethyl 6,6'-dinitrodiphenate, which was attempted by five different methods, in no case yielded dimethyl 6-amino-6'-nitrodiphenate. Instead, the five methods yielded the products listed.

1. A catalytic hydrogenation of dimethyl 6,6'-dinitrodiphenate in benzene over Adams platinum oxide catalyst yielded the dilactam of 6,6'-diaminodiphenic acid.

2. A sodium polysulfide reduction yielded a compound tentatively identified as the cyclic azo or hydrazo derivative of dimethyl 6,6'-dinitrodiphenate solvated with ethanol.

3. Reduction by zinc and ammonium chloride gave both the cyclic azoxy derivative of dimethyl 6,6'-dinitrodiphenate and the cyclic dihydroxamic acid, 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene.

4. A reduction by sodium sulfide and sodium bicarbonate gave the cyclic dihydroxamic acid.

5. From a reduction with tin and hydrochloric acid the same dihydroxamic acid was obtained.

The diacetylated derivative of 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene was prepared in the course of the characterization of the parent compound.

Three mixed Ullmann reactions were tried between a suitably substituted dihalobenzene and a monohalobenzene which was bulkily substituted in both ortho positions. One of these mixed Ullmann reactions was with 2,6-dibromo-1,4-dinitrobenzene and methyl 2-bromo-3-nitrobenzoate. The 2,6-dibromo-1,4-dinitrobenzene was prepared by oxidizing 2,6-dibromo-p-nitroaniline with trifluoro acetic acid and 90 per cent hydrogen peroxide. This recently developed method of oxidizing amines to nitro compounds accomplished the oxidation in good yield and purity.

An attempt was made to prepare 4,6-diiodo-1,3-dinitrobenzene and 2,6-diiodonitrobenzene to serve as intermediates for several mixed Ullmann reactions which were contemplated but never actually carried out. The compounds were to be derived from 4,6-diiodo-m-nitroaniline

and 2,4-diiodo-m-nitroaniline. It has been reported that these diiodo-m-nitroanilines have been prepared by the iodination of m-nitroaniline with iodine monochloride. Therefore, m-nitroaniline was iodinated using a 2:1 molar ratio of iodine monochloride to m-nitroaniline. Some time was spent determining the composition of the resulting iodination products. The product was principally 6-iodo-m-nitroaniline. Other products found were 4-iodo-m-nitroanaline, 4,6-diiodo-m-nitroanaline, 2,6-diiodo-m-nitroaniline, and unidentified white needles which melted at 197.5°-198.5°C. No 2,4-diiodo-m-nitroaniline was found.

Another iodination was tried with a 3:1 molar ratio of iodine monochloride to m-nitroaniline. The product this time consisted principally of 4,6- and 2,6-diiodo-m-nitroaniline. Other products found in smaller amounts were 4-iodo-m-nitroaniline, and three unidentified solids which melted at 197.5°-198.5°C., 207°-210°C., and 234°-235°C.

Chromatography was effectively used for the separation of the products. A silicic acid-chloroform column was employed and elution was by chloroform or a chloroform-methanol mixture.

Mixed Ullmann reactions were attempted with 2,6-dibromo-1,4-dinitrobenzene and methyl 2-bromo-3-nitrobenzoate, and with o-diiodobenzene and methyl 2-bromo-3-nitrobenzoate. The latter reaction was effected both without a diluent and with dimethylformamide as a diluent. Results from several other similarly run Ullmann reactions showed that when dimethylformamide was used as a diluent the yields were slightly lower. The ease of cleanup and purity of product were essentially the same by both methods.

In general, the mixed Ullmann reactions gave unsatisfactory results. The product in each case was found to be a complex mixture,

the separation of which proved to be prohibitively difficult.

By the second general method, the final coupling of bulkily substituted benzene rings was to be accomplished by the decomposition of nitrosoacetylarylamines in the liquid aromatic hydrocarbon to which they were to be coupled. For this approach, certain aromatic amines and diamines were prepared, acetylated, nitrosated, and decomposed in mesitylene. Mesitylene was used as the coupling medium because all the hydrogens on the mesitylene ring are equivalent. Therefore, the coupling of the N-nitroso compound at any position on mesitylene would yield the same product and not a mixture of isomers.

The nitrosations were accomplished with nitrosyl chloride, which has been reported by several workers to be much more effective than nitrous fumes.

The following compounds were nitrosated by nitrosyl chloride and allowed to decompose in mesitylene: 2,6-diacetamidotoluene, 3-acetamido-3'-nitrobimesityl, diacetamidomesitylene, 1,2-diacetamidobenzene, and 2'-nitroacetanilide. The yields were uniformly poor. No product at all was obtained from the run with 2,6-diacetamidotoluene. The run with 2'-nitroacetanilide yielded 2,4,6-trimethyl-2'-nitrobiphenyl, the expected product. This was the only run that yielded a product in sufficient amount and purity to allow an analysis and characterization.

However, in the course of investigating this approach, a new preparation of 2,6-diacetamidotoluene from o-nitrotoluene was developed. The preparations of 2,6-diacetamidotoluene heretofore reported have been long and tedious. It was found that this compound could be prepared by first nitrating o-nitrotoluene to form a mixture of 2,4- and 2,6-dinitro-

toluene. The isomers were not separated but catalytically hydrogenated together over Adams platinum oxide catalyst. Acetylation of the resulting amines by acetic anhydride yielded a mixture of 2,4- and 2,6-diacetamidotoluene. These isomers were then easily separated by a 1:1 acetic acid-water wash. The 2,4-diacetamidotoluene dissolved quickly while the 2,6-diacetamidotoluene dissolved only very slowly.

The approach of the third general method was through the Diels-Alder reaction. 2,3-Dimesityl-1,3-butadiene was prepared and reacted with maleic anhydride. The preparation of 2,3-dimesityl-1,3-butadiene was accomplished by the dehydration of 2,3-dimesityl-2,3-butanediol. The 2,3-dimesityl-2,3-butanediol was in turn prepared by the aluminum amalgam bimolecular reduction of acetomesitylene. The products which were isolated from this bimolecular reduction were the meso and dl forms of 2,3-dimesityl-2,3-butanediol, the cis and trans forms of 2,3-dimesityl-2,3-epoxybutane, and methyl mesityl carbinol. These compounds were efficiently separated by the use of a silicic acid-chloroform chromatographic column.

The dehydration of 2,3-dimesityl-2,3-butanediol yielded a small amount of 3,3-dimesitylbutanone-2 as well as the 2,3-dimesityl-1,3-butadiene. This ketone was one of the two possible products of the pinacol rearrangement of 2,3-dimesityl-2,3-butanediol. 2,3-Dimesityl-1,3-butadiene was also prepared in small amounts by refluxing 2,3-dimesityl-2,3-epoxybutane with glacial acetic acid.

Attempts to resolve the glycols and to interconvert the oxides and glycols through ring opening and closing were unsuccessful.

One attempt was made to add 2,3-dimesityl-1,3-butadiene to maleic

anhydride. Only starting material was recovered which indicated that more stringent conditions must be used.

The steric hindrance encountered in all of the three general methods investigated in this research made the preparation of the desired o- and m-terphenyls extremely difficult. In spite of the difficulties encountered, more information concerning the scope and utility of these methods was obtained. Several unexpected intermediate were characterized and procedures for preparing certain intermediates were modified and improved.

CHAPTER I

INTRODUCTION

The purpose of this research was to explore several synthesis routes which could lead to certain optically active o- and m-terphenyls. Such terphenyls possess unsymmetrically substituted terminal phenyl rings. The rotation of these rings around the bond connecting them to the central ring is restricted due to substituents in their ortho positions (1). Representative types of these terphenyls are illustrated in Figure 1.

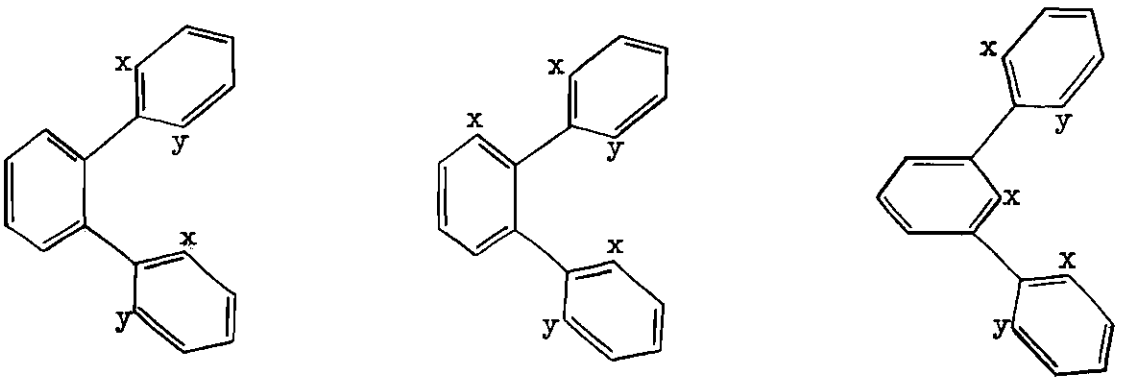

Figure 1. Optically Active Types of o- and m-Terphenyls.

There are two systems used for numbering the positions on ter-

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(1) R. L. Shriner, R. Adams, and C. S. Marvel, Organic Chemistry-An Advanced Treatise, Vol. I, edited by H. Gilman, John Wiley & Sons, Inc., New York, N.Y., 1943, p. 214.

phenyls. Allen and Pingert (2), in their study of the substitution reactions of o-terphenyls, used unprimed numbers for the central ring and primed and double primed numbers for the terminal rings. The system adopted in the publications of the American Chemical Society, however, uses unprimed numbers for one terminal ring, primed numbers for the central ring, and double primed numbers for the remaining terminal ring. This system is used throughout this thesis.

While optical activity due to restricted rotation has been extensively investigated in the biphenyl series, with some extension to p-terphenyl (3), very little similar work seems to have been carried out on o- or m-terphenyl. Adams and Yuan (4) have mentioned possible types of optically active o- and m-terphenyls and the stereoisomeric possibilities of each, but no attempted syntheses of any of these compounds have been reported.

In the present work, three general methods that seemed promising for the preparation of terphenyls were explored. The first general method made use of the Ullmann reaction as a means of coupling the bulky aromatic rings. The Ullmann reaction was the most satisfactory method that Adams (3) found for coupling highly substituted aromatic rings in his preparations of the biphenyl series.

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(2) C. F. H. Allen and F. P. Pingert, J. Am. Chem. Soc., 64, 1365 (1942).

(3) R. Adams and H. M. Teeter, J. Am. Chem. Soc., 62, 2188 (1940) and previous papers of this series.

(4) R. Adams and H. C. Yuan, Chem. Revs., 12, 261 (1933).

Shuttleworth, Rapson, and Stewart (5) have reported the preparation of o-terphenyl-2,2"-dicarboxylic acid. It was obtained in 11.0 per cent yield by the Ullmann coupling of ethyl 2'-iodobiphenyl-2-carboxylate and ethyl o-iodobenzoate, followed by hydrolysis. This compound seems to have more hindrance to free rotation than any other o-terphenyl recorded in the literature.

The Ullmann coupling of 2,6-dibromo-4-nitroiodobenzene gave most surprising and unusual products (6). Besides the "normal" symmetrical product, an unsymmetrical biphenyl, 2,3',6-tribromo-2'-iodo-4,5'-dinitrobiphenyl, and a m-terphenyl, 2,2",6,6"-tetrabromo-2'-iodo-4,4",5'-trinitro-m-terphenyl, were obtained. The latter two compounds were obtained in 20.0 and 4.0 per cent respectively. The unexpected m-terphenyl appears to have been formed from the coupling of the unsymmetrical biphenyl with the starting material. The restriction of rotation in 2,2",6,6"-tetrabromo-2'-iodo-4,4",5'-trinitro-m-terphenyl is greater than in any other m-terphenyl reported in the literature.

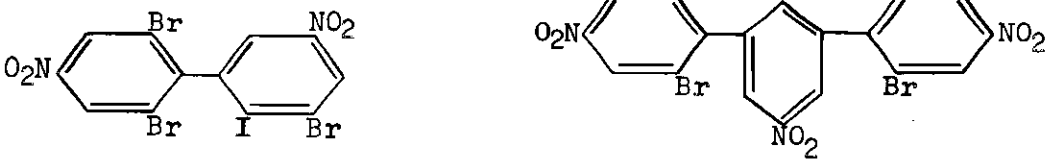

Figure 2. The Unsymmetrical Biphenyl and m-Terphenyl Obtained from the Ullmann Coupling of 2,6-Dibromo-4-nitroiodobenzene.

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(5) R. G. Shuttleworth, W. S. Rapson, and E. T. Stewart, J. Chem. Soc., 1944, 71.

(6) R. B. Carlin and E. A. Swakon, J. Am. Chem. Soc., 77, 966 (1955).

Kornblum and Kendall (7) have investigated the use of dimethylformamide as a diluent for the Ullmann reaction. The unusual solvent power and water solubility of this reagent were attractive enough properties to invite its use in this work, sometimes competitively with an Ullmann reaction using no solvent.

Occasionally the Ullmann reaction fails to give satisfactory results. So it was with the attempted coupling of iodomesitylene by Moyer and Adams (8). Iodomesitylene, with bulky electron-donating methyl groups in both positions ortho to the halide, was treated with copper powder. The yield of bimesityl was only a few per cent. Bimesityl was finally obtained in 22 per cent yield by treating mesitylmagnesium bromide with cupric chloride.

When N-nitrosoacetylarylamines are allowed to decompose in a liquid aromatic hydrocarbon, coupling of the aromatic molecules may take place (9). This approach to the preparation of terphenyls was the second general method explored. While this method has been widely used to prepare substituted biphenyls, it has been used for the preparation of only a few terphenyls.

France, Heilbron, and Hey (10) decomposed N-nitroso-3-acetylaminobiphenyl in benzene to obtain m-terphenyl in 63 per cent yield.

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(7) N. Kornblum and D. L. Kendall, J. Am. Chem. Soc., 74, 5782 (1952).

(8) W. W. Moyer and R. Adams, J. Am. Chem. Soc., 51, 630 (1929).

(9) W. E. Bachmann and R. A. Hoffman, Organic Reactions, Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1949, p. 224.

(10) H. France, I. M. Heilbron, and D. H. Hey, J. Chem. Soc., 1939, 1288.

These workers (11) later allowed the N-acetyl-N-nitroso derivative of m-phenylenediamine to decompose in benzene, whereby they obtained m-terphenyl in 23 per cent yield.

The use of nitrosyl chloride as the nitrosating agent in this reaction has been reported as effecting the nitrosation of certain hindered acetamido groups that previously had resisted nitrosation by the older nitrous fumes method (11). In all cases reported, the use of nitrosyl chloride improved the purity and yield of the product.

Recently this reaction has been applied to the preparation of o-terphenyls. Case (12) reported the decomposition of the N-acetyl-N-nitroso derivative of 2-amino-5-nitrobiphenyl in benzene to yield 5'-nitro-o-terphenyl in 9 per cent yield.

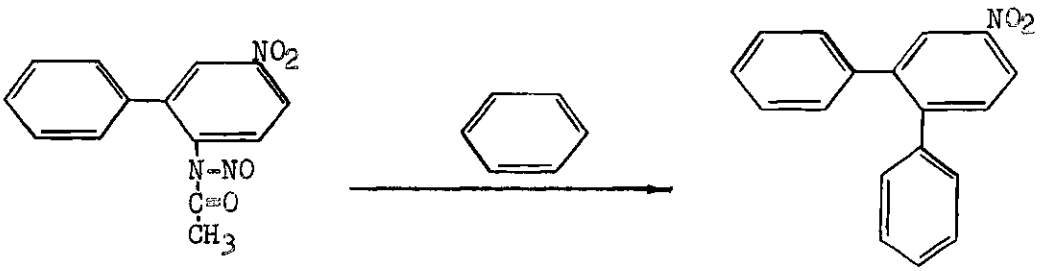

Figure 3. The Preparation of 5'-Nitro-o-terphenyl.

Diels-Alder reactions appear to be promising methods for the preparation of terphenyls. This was the third general method explored in the present research.

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(11) H. France, I. M. Heilbron, and D. H. Hey, J. Chem. Soc., 1940, 369.

(12) F. H. Case, J. Org. Chem., 21, 477 (1956).

When cyclopentadienone is added to an acetylene, a carbonyl-bridged ring is formed. The adduct loses carbon monoxide on heating and forms an aromatic ring. Representative of this type reaction are the following reported by Allen and VanAllan (13)(14). The addition of 2,5-dimethyl-3,4-diphenylcyclopentadienone to acetylene gave a 51 per cent yield of 3',6'-dimethyl-o-terphenyl. The same diene added to dimethyl acetylenedicarboxylate gave a 90 per cent yield of dimethyl 3',6'-dimethyl-o-terphenyl-4',5'-dicarboxylate.

The addition of a diarylbutadiene to an activated olefin, followed by dehydrogenation of the resultant diarylcyclohexene, is a convenient method of synthesizing a large number of substituted terphenyls. m-Terphenyl derivatives may be prepared from 1,3-diarylbutadienes and o-terphenyl derivatives may be prepared from 1,2- and 2,3-diarylbutadienes. Thus, the addition of 1,2-diphenylbutadiene to maleic anhydride followed by hydrolysis and dehydrogenation with sulfur yielded o-terphenyl-3',4'-dicarboxylic acid (15). Similarly, the addition of 2,3-diphenylbutadiene to maleic anhydride, likewise followed by hydrolysis and dehydrogenation with sulfur yielded o-terphenyl-4',5'-dicarboxylic acid (16).

There are several other well-regarded methods that have been used for preparing terphenyls that were not explored during this research.

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(13) C. F. H. Allen and J. VanAllan, J. Am. Chem. Soc., 64, 1260 (1942).

(14) C. F. H. Allen and J. VanAllan, J. Org. Chem., 10, 333 (1945).

(15) K. Alder, J. Hayden, K. Heimbach, K. Neufang, G. Hansen, and W. Gerhard, Ann., 586, 110 (1954).

(16) K. Alder and J. Hayden, Ann., 570, 201 (1950).

Synthesis of terphenyls by the Michael reaction initially involves the addition of β-keto esters to chalcones. The resulting carbethoxycyclohexenone is first treated with a Grignard reagent, then dehydrogenated to give the terphenyl. For example, 2',4',5'-trimethyl-m-terphenyl has been prepared in 15 per cent yield by addition of ethyl β-oxopentanoate to dypnone, followed by treatment with methylmagnesium iodide and dehydrogenation (17).

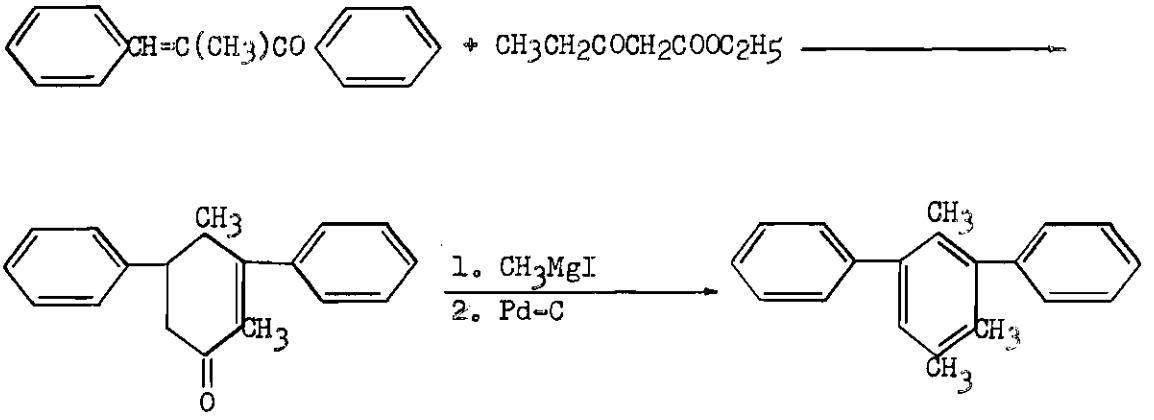

Figure 4. The Preparation of 2',4',5'-Trimethyl-m-terphenyl.

By another method that has been used successfully for terphenyl preparations, quinonoid and hydroquinonoid terphenyls are first obtained. Typically, a benzoquinone or benzoquinone derivative is treated with a diazonium salt or an N-nitrosoacetanilide. Thus, Borsche (18) prepared 2,6-diphenylbenzoquinone monooxime from benzoquinone monooxime and benzenediazonium chloride. Borsche carried the synthesis no further

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(17) F. Langer and F. Wessely, Monatsh., 86, 887 (1955).

(18) W. Borsche, Ann., 312, 211 (1900).

than this, but hydrolysis and reduction could result in the terphenyl.

A condensation method, which might be rewarding if more fully exploited, afforded 2'-hydroxy-5'-nitro-m-terphenyl in 95 per cent yield. This compound was synthesized by Hill (19) who condensed dibenzyl ketone with nitromalondialdehyde.

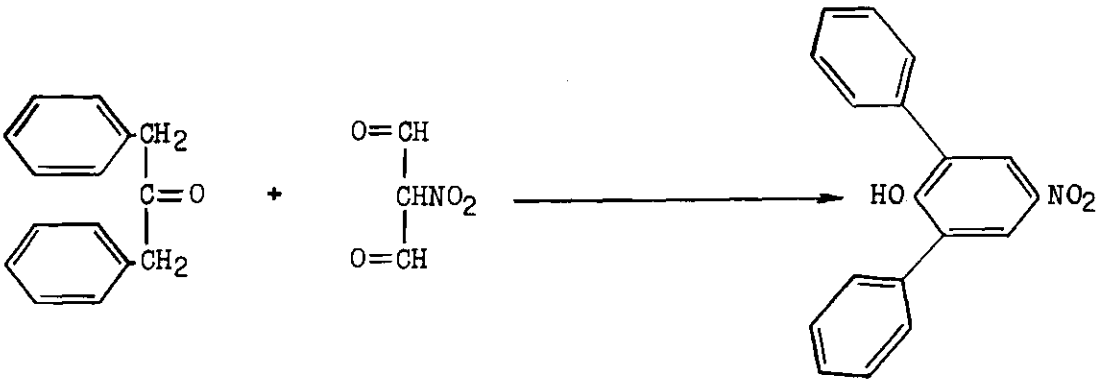

Figure 5. The Preparation of 2'-Hydroxy-5'-nitro-m-terphenyl.

These methods, and others less familiar and less investigated, have been used successfully to prepare a wide variety of substituted o- and m-terphenyls. It should be noticed, however, that the substitutions are commonly on the central benzene ring and very rarely on the terminal phenyl rings. Even more rarely are the substitutions in the 2 or 6 positions of the terminal rings. It was, therefore, the object of this research to explore the possibilities of several different methods for the preparations of these latter types of terphenyls.

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(19) H. B. Hill, Ber., 33, 1241 (1900).

CHAPTER II

EXPERIMENTAL DISCUSSION

Attempted Syntheses of ortho- and meta-Terphenyls Possessing Restricted Rotation By Routes Which Utilize The Ullmann Reaction

The Attempted Preparation of Trimethyl 2,2"-Dinitro-o-terphenyl-3',6,6"-tricarboxylate.--The sequence of reactions connected with this preparation is shown in Figure 6. The dotted lines indicate the desired route. The solid lines indicate the actual steps.

In the third step of this sequence, the esterification of 2-bromo-3-nitrobenzoic acid was easily accomplished in 96 per cent yield by refluxing the acid in methanol saturated with hydrogen chloride. It was also noted that this acid could be esterified by the oxocarbonium ion method, in which the acid was dissolved in 100 per cent sulfuric acid and this solution slowly poured, with stirring, into an exces of cold, dry methanol. After standing for a day, the methanolic solution was poured into an excess of water. The ester was removed by filtration, washed with sodium carbonate solution, then with water and dried at 110°C. While its purity was comparable to the ester prepared by the Fischer method above, the yield was from 30 to 40 per cent lower.

The Ullmann coupling of the next step was performed both without the use of a solvent and with the use of dimethylformamide as a solvent. A 72 per cent average yield from three attempts was realized from the reaction run without a solvent compared with a 56 per cent yield from one run using the dimethylformamide. It was observed that the activation

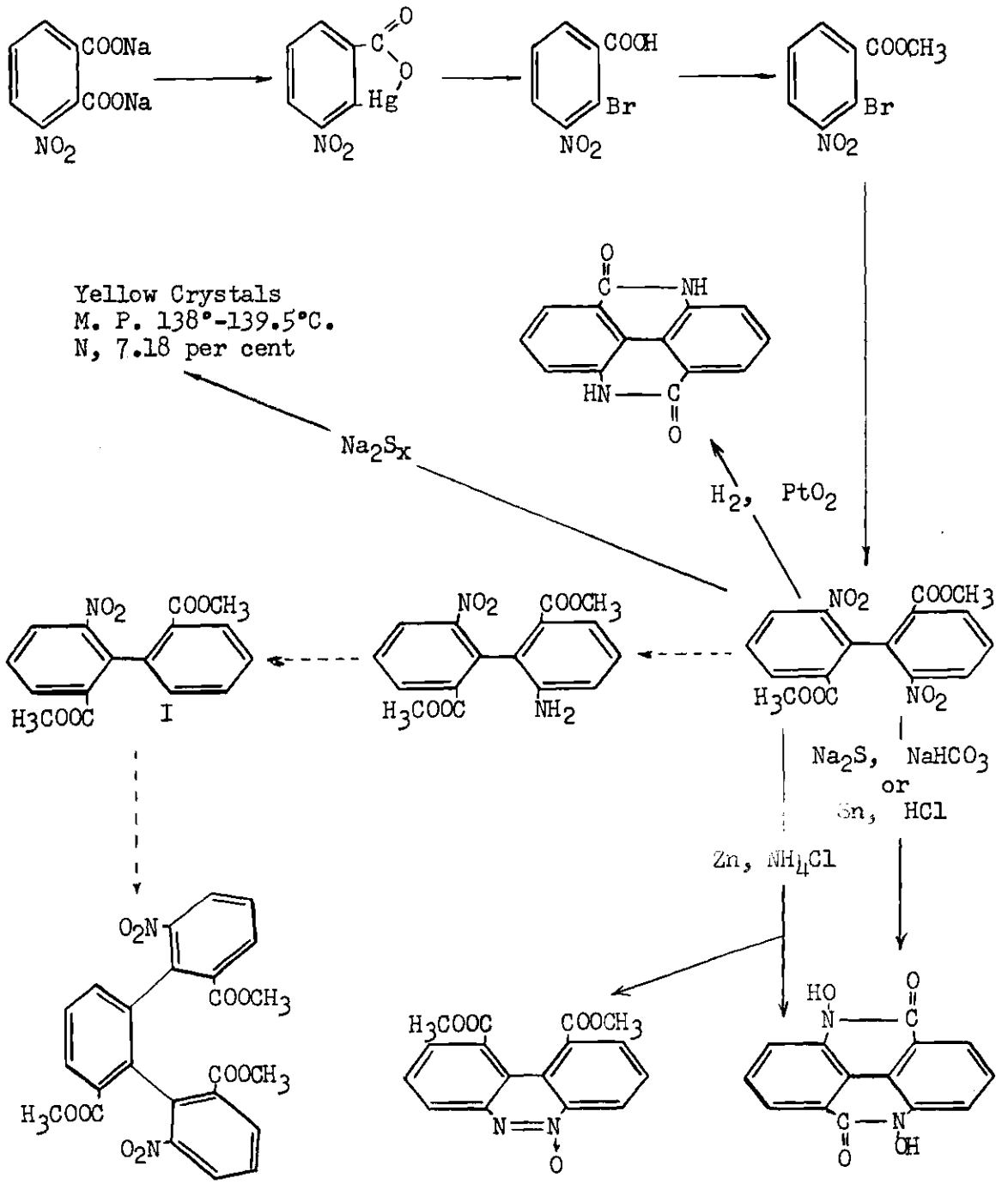

Figure 6. Attempted Synthesis of Trimethyl 2,2"-Dinitro-o-terphenyl-3',6,6"-tricarboxylate.

of the copper powder had to be performed carefully or large amounts of an orange oil would be formed in the reaction mixture and the yield would be greatly lowered. In particular, the final washing of the copper powder with acetone had to be continued until the washings caused no cloudiness when poured in water.

The next step, the selective reduction of dimethyl 6,6'-dinitrodiphenate, was to yield dimethyl 6-amino-6'-nitrodiphenate. The reduction was attempted with sodium polysulfide employing the method that Purdie (20) used successfully to reduce 2,2'-dinitrobiphenyl to 2-amino-2'-nitrobiphenyl.

Most reported reductions of 2-nitrobiphenyls substituted in the adjacent 2' position with an acid or ester group have resulted in lactam formation (21),(22). Thus, Kenner and Stubbings (23) reduced 6,6'-dinitrodiphenic acid with stannous chloride and hydrochloric acid and obtained the dilactam of 6,6'-diaminodiphenic acid. On the other hand, reduction of the ethyl ester of 6,6'-dinitrodiphenic acid under similar conditions, except that the temperature was held below 40°C., yielded not only the dilactam, but about 20 per cent of a "basic oily substance" which slowly solidified. This solid analyzed for a carbethoxyaminophenanthridone. This led these investigators to believe that of the two sets of adjacent carbethoxy and amino groups (formed by the reduction), only one condensed to a lactam.

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(20) D. Purdie, J. Am. Chem. Soc., 63, 2276 (1941).

(21) R. S. Theobald and K. Schofield, Chem. Revs., 46, 171 (1950).

(22) L. Oyster and H. Adkins, J. Am. Chem. Soc., 43, 208 (1921).

(23) J. Kenner and W. V. Stubbings, J. Chem. Soc., 119, 593 (1921).

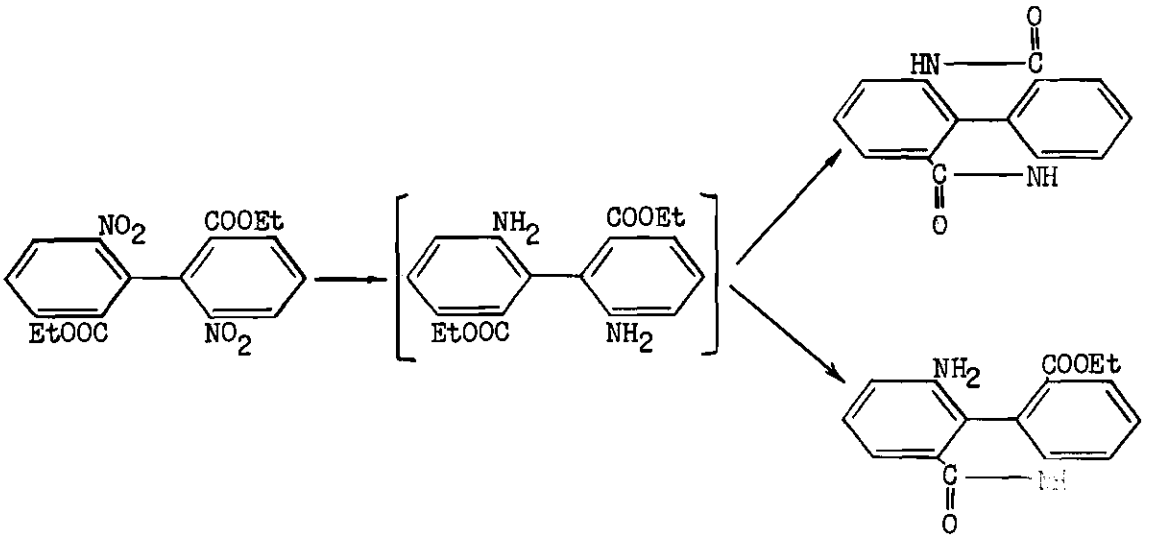

Figure 7. Kenner and Stubbings Reduction of Diethyl 6,6'-Dinitrodiphenate.

It is also known that lactam formation will occur in strongly basic media. Grabe and Wander (24) formed phenanthridone while trying to obtain 2'-amino-2-biphenylcarboxylic acid by a Hofmann reaction on 2'-amido-2-biphenylcarboxylic acid.

In the present work, it was hoped under the mild conditions of a sodium polysulfide reduction that dimethyl 6-amino-6'-nitrodiphenate might be obtained. Several trials were unsuccessful but finally one yielded 0.1 g. of a yellow crystalline material, melting at 138.5°-139.5°C., from 3.0 g. of dimethyl 6,6'-dinitrodiphenate. The yellow crystals analyzed 7.18 per cent nitrogen. This is far too low for dimethyl 6-amino-6'-nitrodiphenate. In fact, if two nitrogen atoms are assumed to be on the molecule, and if the 7.18 per cent nitrogen content is correct, the molecular weight of this material would have to be about

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(24) C. Grabe and C. A. Wander, Ann., 276, 245 (1893).

390. Since dimethyl 6,6'-dinitrodiphenate has a molecular weight of 360, this is a molecular weight greater by 30 than the starting material. This yellow crystalline product could not be diazotized, which is further evidence that reduction to the amine did not take place. Since the crystals had been dried by placing them in an oven at 110°C. and not in a vacuum oven, the simplest assumption to account for a molecular weight greater than the starting material is that of solvent of crystallization. This assumption allows several possibilities. Two molecules of ethanol bound to each of the following compounds analyzes for nitrogen as shown.

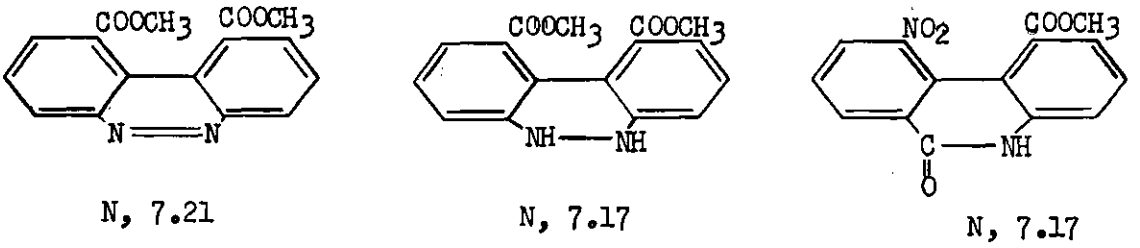

Figure 8. Possible Reduction Products of Dimethyl 6,6'-Dinitrodiphenate.

Since 9(10)phenanthridone itself is known to be a compound which melts at 293°C., the 4-carbomethoxy-5-nitrophenanthridone shown solvated with ethanol is not likely to be a material melting at 138.5°-139.5°C. Certainly more chemical evidence, or infrared examination, is needed to determine the identity of these yellow crystals. But it can be said that the cyclic azo and hydrazo compounds solvated with ethanol are likely possibilities.

A series of reductions in different media was then conducted to see if under other conditions dimethyl 6-amino-6'-nitrodiphenate might

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(24) C. Grabe and C. A. Wander, Ann., 276, 245 (1893).

be isolated. The first of these was a method employing sodium sulfide and sodium bicarbonate by which Hodgson and Ward (25) were able to reduce selectively several polynitro naphthalenes that previously had resisted reduction. A neutral medium reaction using zinc and ammonium chloride was also tried as well as a non-aqueous catalytic hydrogenation using Adams platinum oxide catalyst. None of these methods yielded dimethyl 6-amino-6'-nitrodiphenate. All yielded, at least for one product, a white amorphous solid having certain properties in common with the dilactam of 6,6'-diaminodiphenic acid as described by Kenner and Stubbings. Thus, the solids did not melt but burned upon being heated in an open flame. They were insoluble in the usual organic solvents and could not be diazotized. To compare these solids with known 6,6'-diaminodiphenic acid dilactam, some dimethyl 6,6'-dinitrodiphenate was totally reduced by tin and hydrochloric acid in order to obtain the same product that Kenner and Stubbings had isolated. A white amorphous solid was obtained from this reduction also. Actually, Kenner and Stubbings used stannous chloride and hydrochloric acid but tin and hydrochloric acid was expected to yield the same product. Since the non-melting products from the several reductions could not be compared by melting points, infrared spectra were taken of the white solids obtained from the zinc and ammonium chloride reduction, the sodium sulfide and sodium bicarbonate reduction, and the catalytic hydrogenation and compared with the spectrum of the product from the tin and hydrochloric acid reduction of dimethyl 6,6'-dinitrodiphenate.

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(25) H. H. Hodgson and E. R. Ward, J. Chem. Soc., 1945, 794.

While the spectra of the white solids from the sodium sulfide and sodium bicarbonate method, the zinc and ammonium chloride method, and the tin and hydrochloric acid method showed a few slight differences, they were very similar. However, the spectrum of the product from the catalytic hydrogenation was decidedly different from the others. Oddly enough, evidence arising from subsequent tests indicated this material, rather than the product from the tin and hydrochloric acid reduction, to be the dilactam of 6,6'-diaminodiphenic acid. Thus, it was proved to be a chemically neutral compound. Boiling acetic anhydride failed to acetylate it as evidenced by identical infrared spectra of the materials before and after treatment by the acetic anhydride. According to Theobald and Schofield (21), the lactam of 2'-amino-2-biphenylcarboxylic acid (phenanthridone) cannot be acetylated. If this is so, the dilactam of 6,6'-diaminodiphenic acid would not likely be acetylated either. A solution of the catalytic hydrogenation product in concentrated sulfuric acid fluoresced deep blue under ultraviolet light, and from this solution, upon careful dilution with water, fine yellow needles were deposited. These needles could be further purified by sublimation. All of this behavior was described by Kenner and Stubbings as that of 6,6'-diaminodiphenic acid dilactam. Finally, the nitrogen analysis of 11.78 per cent found for the sublimed yellow needles checked well with the 11.86 per cent calculated for 6,6'-diaminodiphenic acid dilactam.

On the other hand, evidence from subsequent tests indicated the white solids from the zinc and ammonium chloride reduction, the tin and hydrochloric acid reduction, and the sodium sulfide and sodium bicarbonate reduction to be cyclic hydroxamic acids. Complete analysis of the

zinc and ammonium chloride reduction product checked very close to that calculated for the cyclic hydroxamic structure. This analysis was assumed applicable to the white solids from the tin and hydrochloric acid reduction and the sodium sulfide and sodium bicarbonate reduction since by identical chemical behavior and close agreement of their infrared spectra they were judged to be identical compounds. Boiling acetic anhydride reacted with each of these three products to give white solids which possessed identical infrared spectra consistent with an acetylated product. Complete analysis of one of these compounds (the acetylated product from the zinc and ammonium chloride reduction) checked very closely with the values calculated for the proposed acetylated hydroxamic acid structure. Further, these solids proved themselves to be acidic by dissolving appreciably in 10 per cent sodium hydroxide solution.

A curious phenomenon occurred upon neutralizing the basic solution with mineral acid. Part of the precipitated material was an amorphous white solid which could be acetylated and hence judged to be the regenerated hydroxamic acid. But an appreciable amount of the precipitated material was a dull red amorphous solid which could not be acetylated by boiling acetic anhydride. A red solid of the same appearance could be formed also by the action of boiling glacial acetic acid on the white cyclic hydroxamic acids. Under the action of this reagent the white solid was rapidly converted to a flocculent dull red solid. The identity of this red solid was not pursued.

One more product was isolated from the reduction of dimethyl 6,-6'-dinitrodiphenate by the zinc and ammonium chloride method. This product, a yellow crystalline material melting at 184°-185°C., was obtained

in very small yield. While an hydroxylamine would normally be expected from a zinc and ammonium chloride reduction of a nitro group, the yellow crystals resisted oxidation to the expected nitroso compound. It could not be acetylated or dizaotized, hence it was not likely a mono- or diamine. In its infrared spectrum, the nitro group absorption bands present in the spectrum of dimethyl 6,6'-dinitrodiphenate had disappeared, but the original ester carbonyl absorption band remained unmoved. This evidence excludes a lactam. A nitrogen analysis of the yellow crystals checked with the value calculated for the cyclic azoxy compound, 1,10-dicarbomethoxybenzo(c)cinnoline-5-oxide. The obtained chemical and infrared evidence supports this conclusion.

Attempts to reduce dimethyl 6,6'-dinitrodiphenate selectively, consistently gave products other than the desired dimethyl 6-amino-6'-nitrodiphenate. Consequently, this synthesis route to trimethyl 2,2"-dinitro-o-terphenyl-3',6,6"-tricarboxylate, which used dimethyl 6-amino-6'-nitrodiphenate as an intermediate, was abandoned.

Attempted Preparation of Dimethyl 2,2',2",5'-Tetranitro-m-terphenyl-6,6'-dicarboxylate.--This second attempted terphenyl preparation was to have been accomplished by a mixed Ullmann reaction using four moles of methyl 2-bromo-3-nitrobenzoate per mole of 2,6-dibromo-1,4-dinitrobenzene.

The product would be a m-terphenyl having restricted rotation, but not di-ortho substituted on all rings. Cis and trans isomers were expected. The cis terphenyl would exist as a meso form and the trans would exist as a dl modification.

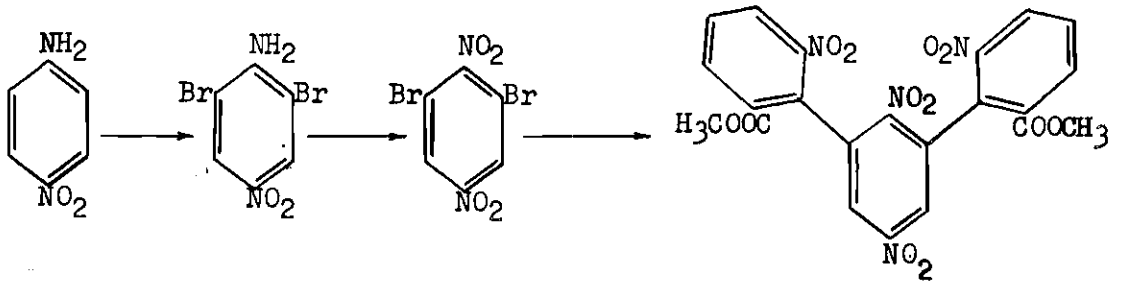

Figure 9. Attempted Route to Dimethyl 2,2',2",5'-Tetranitro-m-terphenyl-6,6'-dicarboxylate.

2,6-Dibromo-p-nitroaniline was prepared easily in excellent yield and purity by Holleman's (26) procedure by the bromination of p-nitroaniline.

The oxidation of 2,6-dibromo-p-nitroaniline to 2,6-dibromo-1,4-dinitrobenzene was based on Emmons (27) method of using peroxytrifluoroacetic acid. While Emmons, for most of his oxidations, generated peroxytrifluoroacetic acid in situ by the use of trifluoroacetic anhydride and 90 per cent hydrogen peroxide, he did oxidize several negatively substituted anilines in reasonably good yields by a mixture of trifluoroacetic acid and 90 per cent hydrogen peroxide. Following the latter procedure, 2,6-dibromo-p-nitroaniline was oxidized to 2,6-dibromo-1,4-dinitrobenzene in 70 per cent yield. Several later attempts to increase the yield by elevating the temperature above the 60°-65°C. range used, and by increasing the amount of hydrogen peroxide and trifluoroacetic acid, resulted only in increasing the amount of accompany-

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(26) A. F. Holleman, Rec. trav. chim., 25, 183 (1906).

(27) W. D. Emmons, J. Am. Chem. Soc., 76, 3470 (1954).

ing tar with no increase in yield of product.

A purification method for fairly large amounts of product was not extensively pursued. Too much gummy tar was produced for decolorizing carbon and recrystallization from ethanol to be effective. The tar could be removed by a cold glacial acetic acid wash although it dissolved an appreciable amount of 2,6-dibromo-1,4-dinitrobenzene. For small amounts of material, chromatography using a column of silicic acid suspended in chloroform was fairly effective in yielding a clean product. From the cleaned product the unreacted amine had to be removed. Surprisingly enough, a room temperature glacial acetic acid trituration of the mixture removed the dinitro compound quickly but dissolved the nitroamine only very slowly and incompletely. In fact, the amine could be recrystallized from glacial acetic acid.

The best scheme for purification was an initial distillation of the product under vacuum, followed by the separation of unreacted amine using glacial acetic acid. Recrystallization of the dinitro compound from ethanol gave a reasonably pure compound.

The mixed Ullmann reaction between methyl 2-bromo-3-nitrobenzoate and 2,6-dibromo-1,4-dinitrobenzene was then attempted. Attempts to separate the reaction products by chromatography, fractional vacuum sublimation and fractional crystallization from ethanol yielded only dimethyl 6,6'-dinitrodiphenate and some unreacted methyl 2-bromo-3-nitrobenzoate. No further attempts at separation were carried out.

Attempted Preparation of Dimethyl 2,2"-Dinitro-o-terphenyl-6,6"-dicarboxylate.--The preparation of this o-terphenyl was attempted by a mixed Ullmann reaction with about two moles of methyl 2-bromo-3-nitro-

benzoate per mole of o-diiodobenzene.

Two stereoisomers could be formed, a cis and a trans compound. The cis compound would be the meso form and the trans isomer would be the dl form.

An Ullmann reaction using no solvent was run as well as an Ullmann reaction using dimethylformamide as solvent. Separation of the reaction products was attempted by steam distillation and fractional crystallization from ethanol. Small amounts of unreacted starting materials plus some dimethyl 6,6'-dinitrodiphenate were isolated from the gummy products obtained from both Ullmann reactions. None of the desired terphenyl, however, was isolated.

Attempted Preparation of 3',6,6"-Trimethyl-2,2"-dinitro-o-terphenyl.-- The route for the preparation of this compound is outlined in Figure 10.

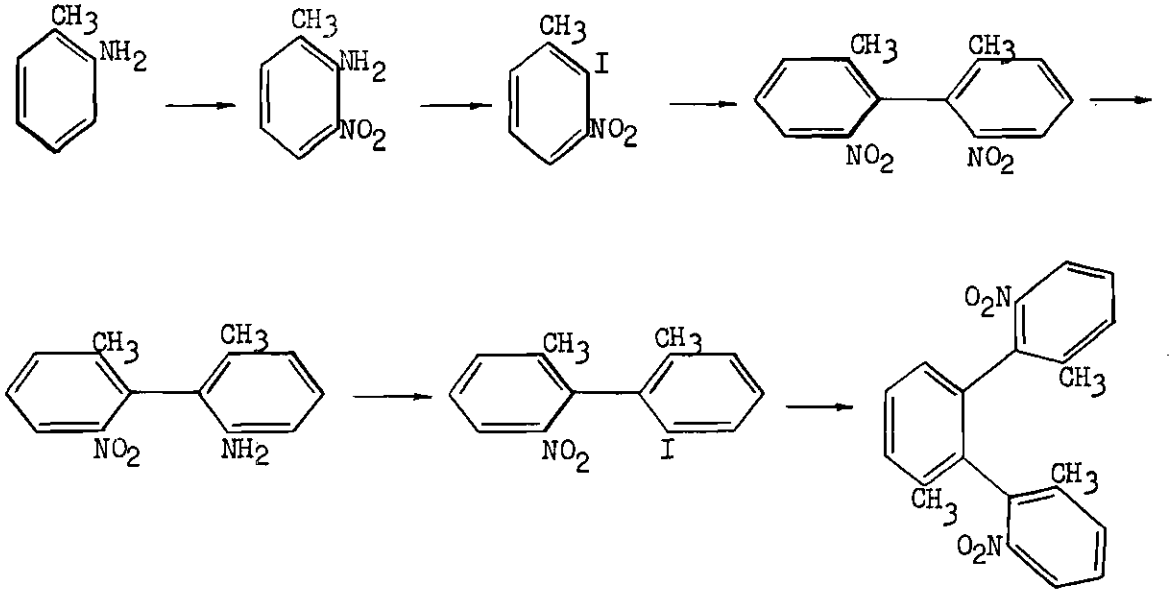

Figure 10. Attempted Route to 3',6,6"-Trimethyl-2,2"-dinitro-o-terphenyl.

For this terphenyl two racemic modifications are possible, one cis and one trans.

The first non-routine step in this synthesis was the Ullmann coupling of 2-iodo-3-nitrotoluene to form 2,2'-dimethyl-6,6'-dinitrobiphenyl. Here a reaction using no solvent was run competitively with a reaction using dimethylformamide as solvent. The purity of product from both methods, as judged by the melting points and appearance, was the same but the method using no solvent gave a 72.5 per cent yield while the method employing dimethylformamide as diluent afforded a 66.7 per cent yield.

The selective reduction of 2,2'-dimethyl-6,6'-dinitrobiphenyl with sodium polysulfide to 2,2'-dimethyl-6-amino-6'-nitrobiphenyl by the method of Purdie (20) yielded 52 per cent of the theoretical. Sako (28) reported that the reduction of this compound by sodium sulfide goes in 73 per cent yield. However, his method was not investigated.

A troublesome step in this synthetic route was the diazotization of 2,2'-dimethyl-6-amino-6'-nitrobiphenyl and the subsequent treatment of the diazonium salt with potassium iodide to give 2,2'-dimethyl-6-iodo-6'-nitrobiphenyl. The best yield realized was 26.2 per cent. One reason for the low yield was a side reaction occurring from the treatment of the diazonium salt with potassium iodide in which 2,2'-bitolyliodonium iodide was formed.

Angeletti (29), who has investigated this and related reactions, states that iodoniumiodide formation is a characteristic reaction of

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(28) Shin-Ichi Sako, Bull. Chem. Soc. Japan, 9, 393 (1934).

(29) A. Angeletti, Gazz. chim. ital., 61, 832 (1931).

2-diazo-2'-substituted biphenyls with potassium iodide, occurring when the 2'-substituting group is N_2Cl, NO_2, Cl, Br, I or OCH_3 but not CH_3.

Another persistent side reaction intervened before the potassium iodide treatment. During the diazotization of the nitroamine considerable amounts of a brown precipitate formed, generally becoming noticeable when the diazotization was about half through. This was believed to be the diazoamino compound.

Many different sets of diazotization conditions were tried in an attempt to eliminate or reduce both of these costly side reactions. Sulfuric acid was substituted for hydrochloric acid as the diazotization acid and was tried in different concentrations as well as using it in the "inverted" method. The nitrosylsulfuric acid method, using phosphoric acid as diluent, also was tried. None of the variations in conditions tried did much to increase the yield or to cut down on the heavy amounts of tar which invariably formed. Separation of the product from the tar was achieved both by vacuum sublimation and steam distillation. Vacuum sublimation seemed to give a cleaner product.

In view of the low yields obtained in this last step and the anticipated difficulty and time to be involved in the Ullmann reaction product separation in the final step, this synthesis route was set aside in favor of a more promising one.

The Iodination of m-Nitroaniline.--In order to obtain several intermediates usable in the preparation of certain terphenyls, m-nitroaniline was iodinated by iodine monochloride. Although the intended syntheses in which these intermediates were to be used were never carried

out, the product composition from this iodination reaction was investigated for the cases in which two and three moles of iodine monochloride were used per mole of m-nitroaniline. During both of the trials, described below, a heavy amount of tar was formed.

It would be expected that the use of different molar proportions of iodine monochloride and m-nitroaniline would alter the kind and proportion of products. This was found to be the case. The use of two moles of iodine monochloride per mole of m-nitroaniline gave as the main product, 6-iodo-m-nitroaniline which separated from the acetic acid reaction mixture upon cooling. The major product obtained upon dilution of the filtered acetic acid was 4,6-diiodo-m-nitroaniline. Smaller amounts of 4-iodo-m-nitroaniline and 2,6-diiodo-m-nitroaniline were also found present. The separation of the three products obtained from the dilution of the acetic acid was achieved satisfactorily only by chromatography. A column of silicic acid suspended in chloroform was used.

Upon making the diluted acetic acid basic the last of the products was obtained, white feathery crystals melting at 197.5°-198.5°C. A compound with this melting point and appearance does not appear in the literature as an iodinated m-nitroaniline. Also, an iodine analysis of 42.8 per cent for these crystals does not check with the 48.1, 65.1 or 73.8 per cent iodine calculated for a mono-, di, or triiodo-m-nitroaniline respectively. An acetylated monoiodo-m-nitroaniline, however, calculates for 41.4 per cent iodine. Certainly, chemical and infrared evidence and a complete analysis of this material are needed for identification, but such an acetylated compound arising from a re-

action of excess hot glacial acetic acid on an amine is a definite possibility.

Three moles of iodine monochloride was then used per mole of m-nitroaniline in an effort to reduce the amount of monoiodinated product and to obtain more diiodinated product. The procedure used was based on a method of Brenans (30).

While preparing the iodine monochloride, through an error in weighing, 15 per cent too much chlorine was added. Whether this had any effect on the nature of the products found is not known.

In contrast to the iodination using two moles of iodine monochloride in which 16.5 grams of 6-iodo-m-nitroaniline precipitated when the reaction cooled, when three moles of iodine monochloride were used no precipitate at all formed upon cooling the reaction. Indeed, even chromatography failed to isolate any 6-iodo-m-nitroaniline. Upon diluting the acetic acid reaction solution with water, a sludge containing five products separated. In spite of the heavy amount of tar, some separation of 4-iodo-m-nitroaniline and 2,6-diiodo-m-nitroaniline was effected by fractional crystallization from ethanol. However, chromatography on a silicic acid and chloroform column was by far the more efficient separation method. By this method 4-iodo-m-nitroaniline, 4,6-diiodo-m-nitroaniline, 2,6-diiodo-m-nitroaniline, yellow crystals melting at 207°-210°C. and a white amorphous material melting at 234°-235°C. were isolated.

The material melting at 207°-210°C. was never obtained in large enough quantity to purify it properly for analysis. The white solid

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(30) P. Brenans, Comptes rend., 138, 1503 (1904).

melting at 234°-235°C. analyzed 63.2 per cent for iodine. This figure neither fits a mono-, di-, or triiodo-m-nitroaniline, nor does it fit the calculated iodine for these compounds acetylated or containing solvent of crystallization. These two products then remain unidentified.

The dilute acetic acid from which these compounds were filtered still contained one more compound. This was a white feathery crystalline solid melting at 197.5°-198.5°C. This solid, mixed with the white crystals melting at 197.5°-198.5°C. obtained from the first trial, did not depress the melting point and was also tentatively identified as an acetylated monoiodo-m-nitroaniline.

Attempts to Synthesize Terphenyls by Routes Incorporating Nitrosoacylarylamines as Intermediates

Introduction.--The synthesis attempts of this section involving the coupling reaction of nitrosoacylarylamines with aromatic hydrocarbons were based on the methods devised by Heilbron, France, Hey, and their collaborators (9)(11). Mesitylene was used as the hydrocarbon coupling medium because all the hydrogens on the mesitylene ring are equivalent. Therefore, the coupling of the N-nitroso compound at any position on mesitylene would yield the same product and not a mixture of isomers. The results obtained from this approach were uniformly poor. The yields were extremely low and the products were very impure. However, more information concerning the scope and limitations of this coupling reaction was obtained, and the syntheses of some difficult to obtain intermediates were improved.

Attempted Preparation of 2,2',2",4,4",6,6"-Heptamethyl-m-terphenyl.--The several investigated routes of synthesis to this compound are outlined in Figure 11.

The development of several routes stemmed from attempts to prepare more easily 2,6-diacetamidotoluene, the key intermediate for the preparation of this terphenyl. Several routes were used which involved selective reduction, by ammonium sulfide, of a nitro group in the para position of polynitrated toluene molecules. These included a five step route starting from o-nitrotoluene and a four step route starting from trinitrotoluene. These routes were shortened one step by the platinum oxide catalyzed hydrogenation of 2,6-dinitrotoluene in the presence of acetic anhydride to give 2,6-diacetamidotoluene directly.

However, the ammonium sulfide reductions in both of these routes were unpleasant, tedious, and time-consuming steps. A much more satisfactory method was devised starting with the nitration of o-nitrotoluene. Rather than separate the 2,4- and 2,6-dinitro isomers they were hydrogenated together and the resulting diamine mixture was diacetylated. The 2,4- and 2,6-diacetamidotoluenes were then easily separated by sublimation or, even easier, by treatment with 1:1 acetic acid. The separation by sublimation depended on the readiness of 2,6-diacetamidotoluene to sublime at its melting point while the 2,4-isomer showed no tendency to sublime at all at these conditions (31). The separation by 1:1 acetic acid was possible since 2,4-diacetamidotoluene proved to be readily soluble in this reagent at room temper-

(31) A. G. Green and T. A. Lawson, J. Chem. Soc., 59, 1013 (1891).

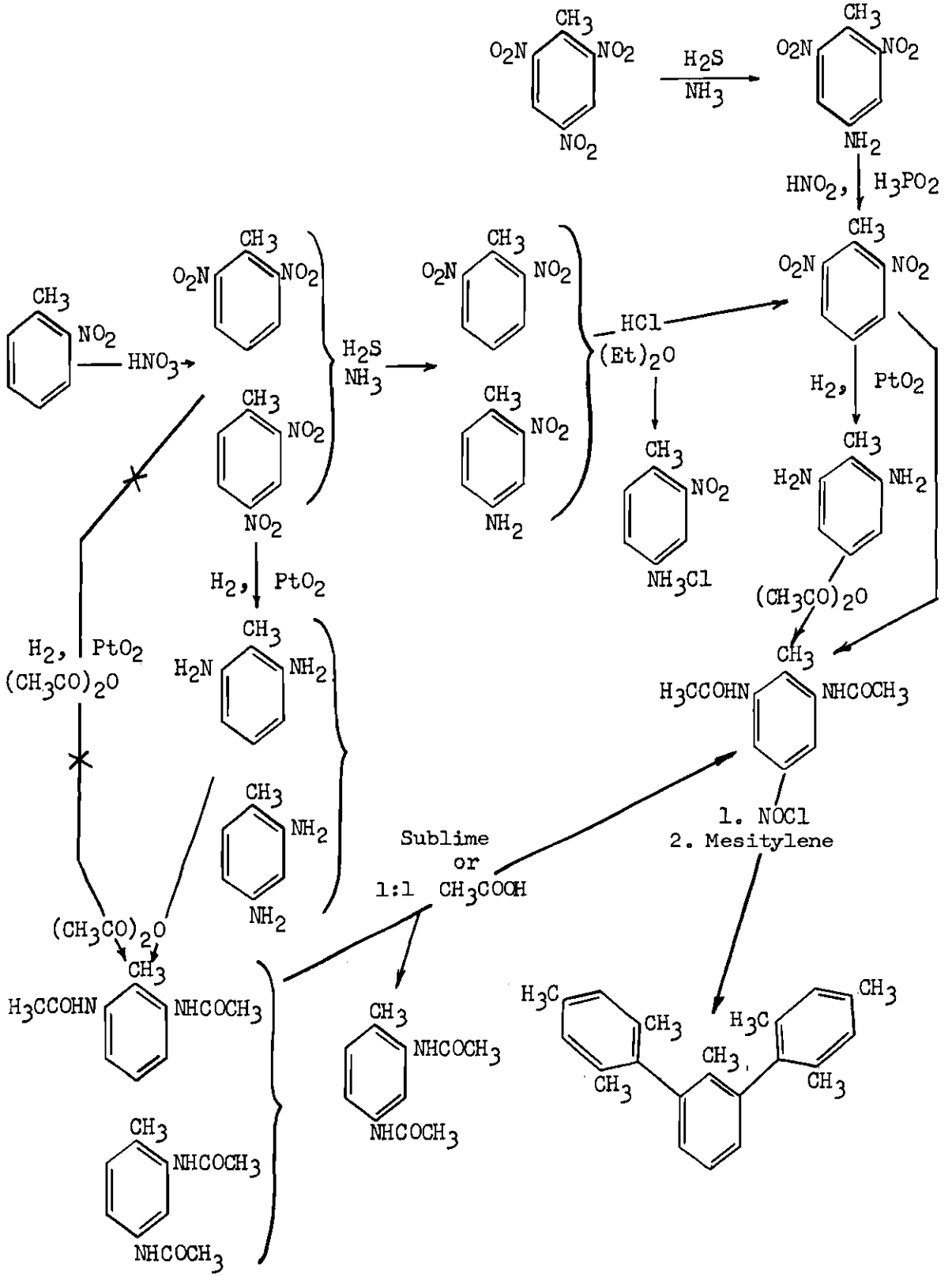

Figure 11. Attempted Routes to 2,2',2",4,4",6,6"-Heptamethyl-m-terphenyl.

ature while 2,6-diacetamidotoluene was only very slightly so.

An attempt was made to achieve a two step synthesis of 2,6-diacetamidotoluene from o-nitrotoluene by a platinum oxide catalyzed hydrogenation of the mixture of 2,4- and 2,6-dinitrotoluene in the presence of acetic anhydride. Unfortunately, the one attempt performed failed, an intractable oil being formed. This failure was surprising in view of the facile reduction and acetylation of 2,6-dinitrotoluene by itself.

The attempt to nitrosate 2,6-diacetamidotoluene with nitrosyl chloride and couple the nitroso compound with mesitylene to form the terphenyl was done in one step. However, a thick oil was the only material isolated from the reaction.

Attempted Preparation of 2,2',2",4,4',4",6,6',6"-Nonamethyl-3-nitro-m-terphenyl.--The route attempted for this preparation is outlined in Figure 12.

This route involved the synthesis of 3,3'-dinitrobimesityl. To prepare this compound, two methods were tried to nitrate bimesityl. One method, that of Adams and Joyce (32), was satisfactory but it necessitated the preparation of 100 per cent nitric acid. A simpler method was adapted from that described by Powell and Johnson (33) for the mononitration of mesitylene by acetic anhydride and fuming nitric acid. This adaptation proved simpler and gave just as satisfactory results as that of Adams and Joyce.

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(32) R. Adams and R. M. Joyce, J. Am. Chem. Soc., 60, 1489 (1938).

(33) G. Powell and F. R. Johnson, Organic Syntheses, Coll. Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1957, p. 449.

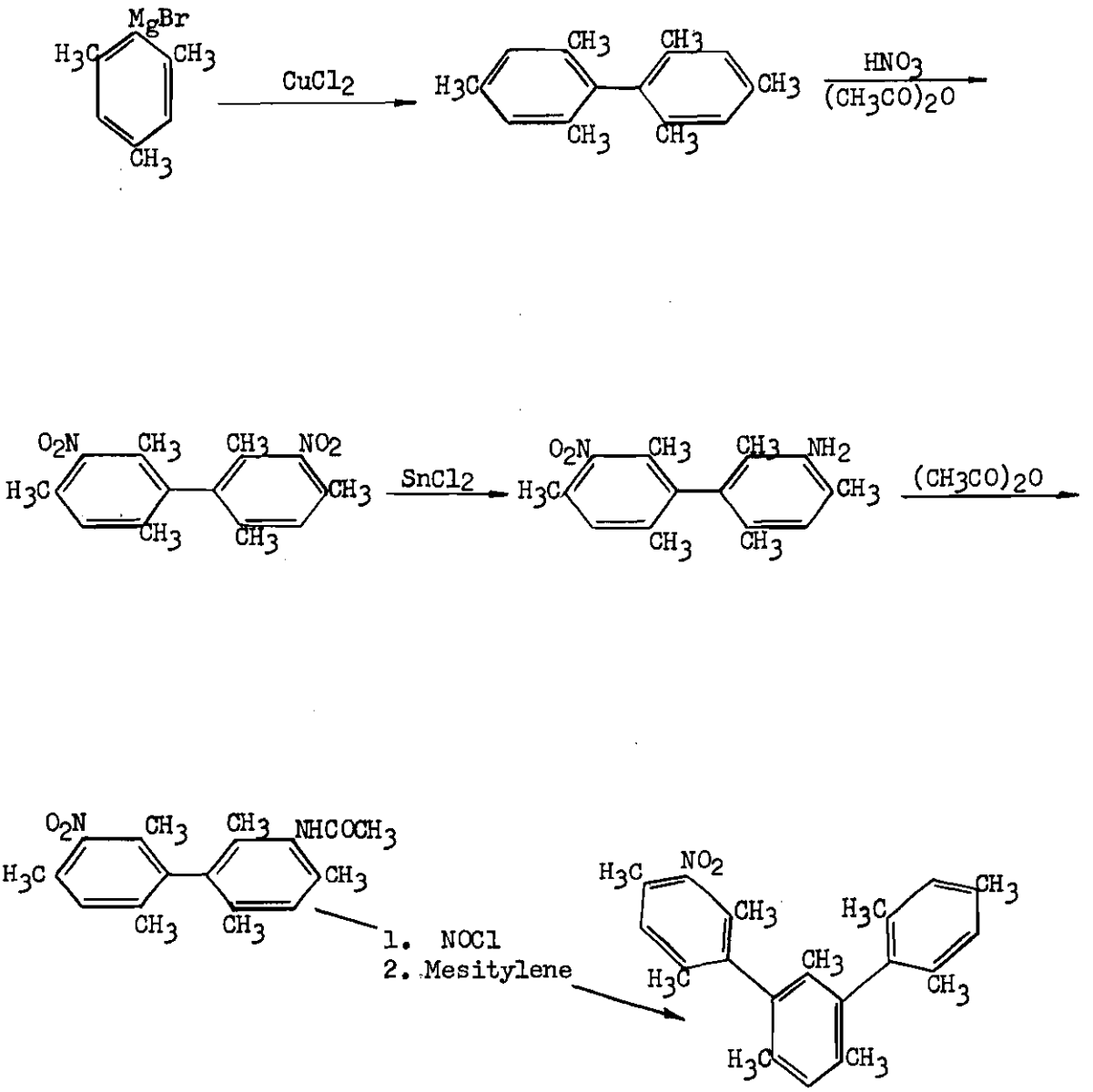

Figure 12. Attempted Preparation of 2,2',2",4,4',4",6,6',6"-Nonamethyl-3-nitro-m-terphenyl.

The nitrosation of 3-acetamido-3'-nitrobimesityl, a subsequent intermediate, and the coupling of its nitroso compound with mesitylene produced a waxy gum. None of the desired terphenyl could be isolated from it.

Attempted Preparation of 2,2',2",4,4',4",6,6'6"-Nonamethyl-m-terphenyl.--The route attempted for this preparation is outlined in Figure 13.

It was necessary to prepare diacetamidomesitylene for this route. Hence, in the third step, diaminomesitylene was diacetylated by acetic anhydride and pyridine according to the method of Adams and Chase (34). The material obtained, however, melted at 340°-345°C., which does not agree with the 320°-325°C. melting range reported by Adams and Chase.

The nitrosation of diacetamidomesitylene and the subsequent coupling reaction yielded a white solid melting at 165.0°-167.5°C. This product seemed to be a mixture of close melting compounds and was never obtained pure enough for analysis.

Attempted Preparation of 2,2',4,4',6,6'-Hexamethyl-o-terphenyl.--The two attempted synthesis routes to this compound are shown in Figure 14.

The nitrosation of 1,2-diacetamidobenzene and the coupling of the nitroso compound with mesitylene yielded a quantity of impure product only large enough to take a melting point. Therefore, the four step synthetic route shown was attempted; however, this was stopped after the first step in view of the yield obtained from that step and the anticipated yields of following steps. The product obtained from

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(34) R. Adams and R. G. Chase, J. Am. Chem. Soc., 70, 4202 (1948).

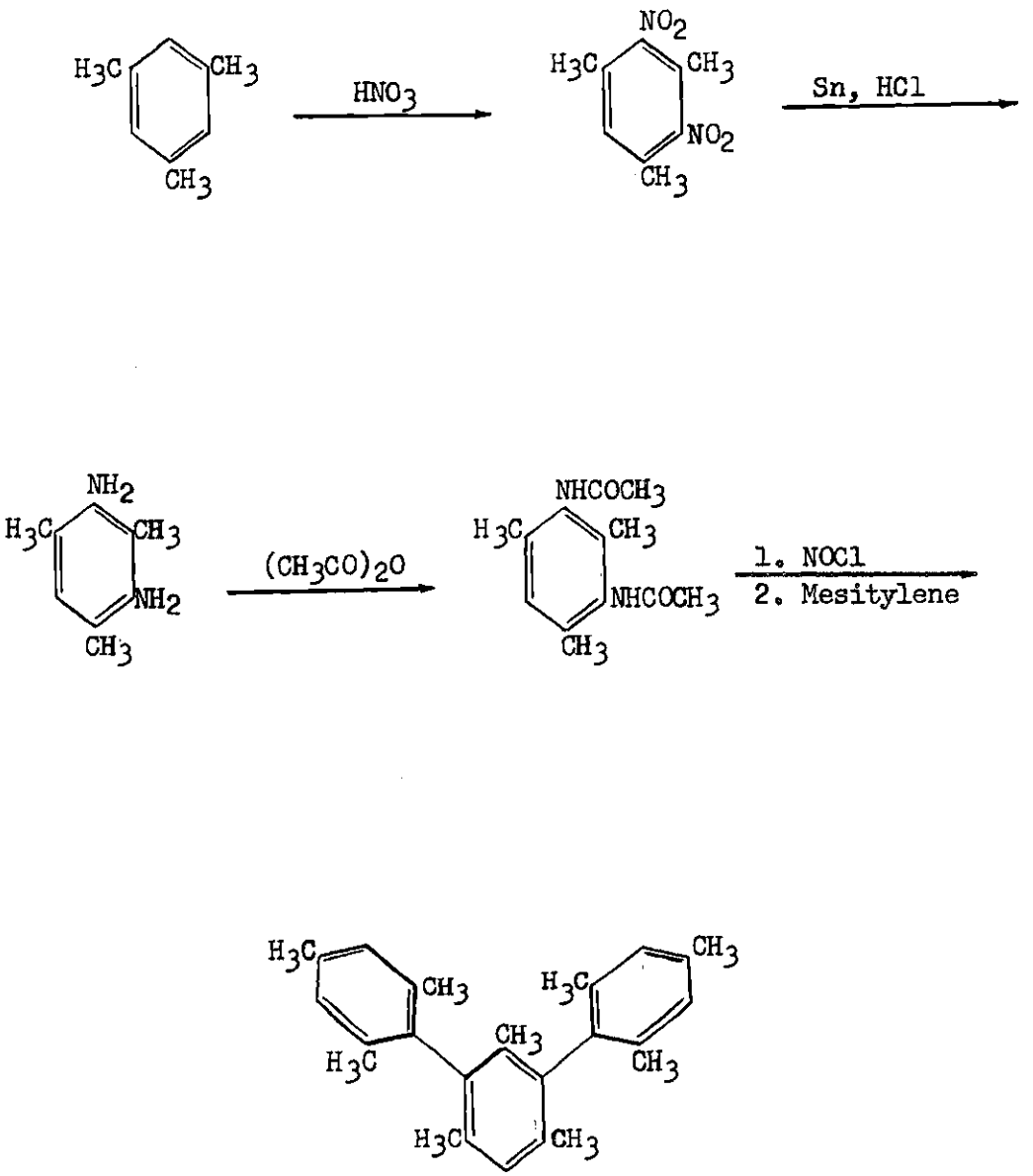

Figure 13. Attempted Preparation of 2,2',2",4,4',4",6,6',6"-Nonamethyl-m-terphenyl.

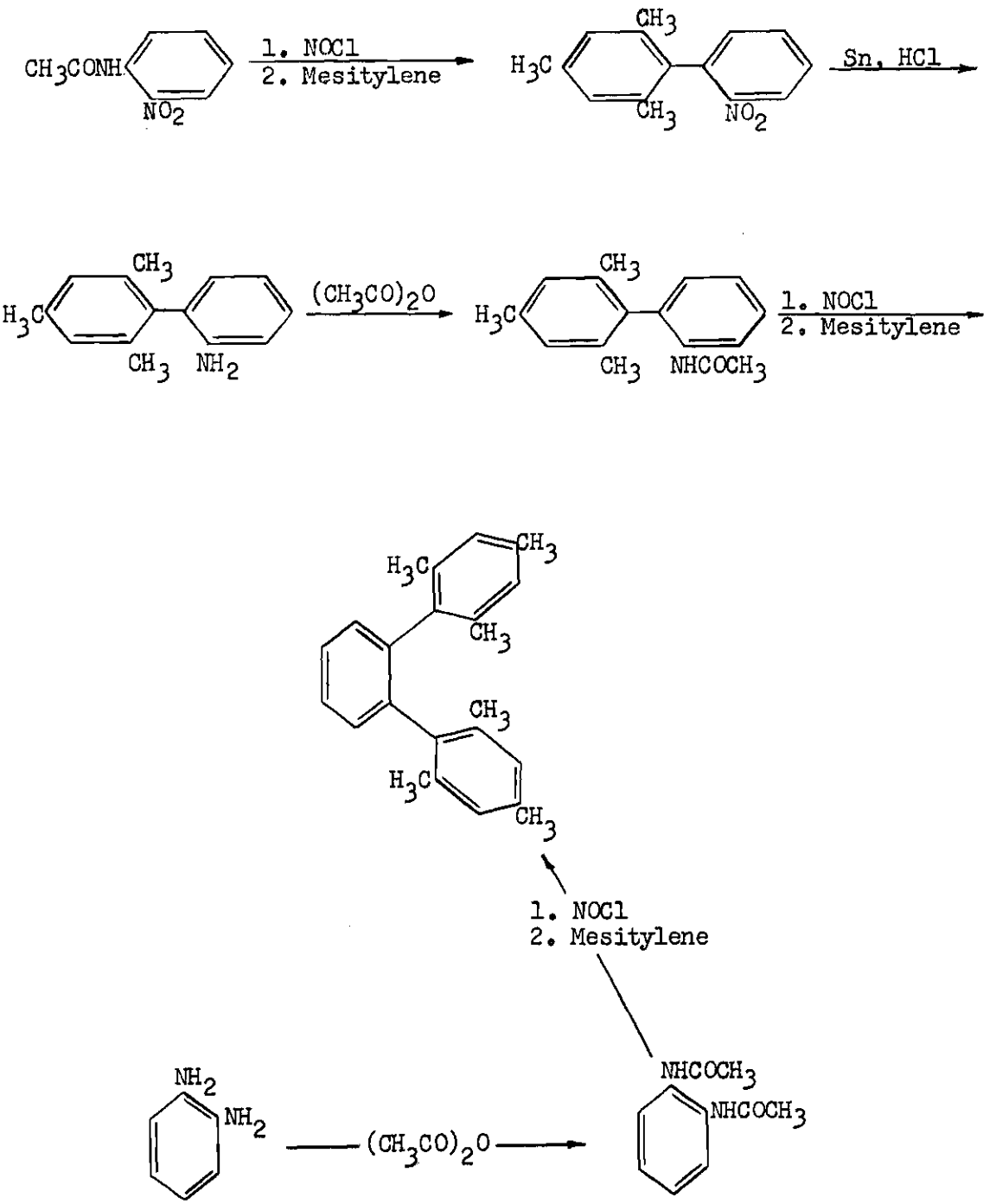

Figure 14. Attempted Routes to 2,2",4,4",6,6"-Hexamethyl-o-terphenyl.

the first step was a yellow solid which melted at 64°-65°C. and analyzed for nitrogen satisfactorily for the value calculated for 2,4,6-trimethyl-2'-nitrobiphenyl, the expected product.

Synthesis Methods Utilizing the Diels-Alder Reaction

Attempted Preparation of 2,2",4,4",6,6"-Hexamethyl-o-terphenyl-4',5'-dicarboxylic Acid.--While this terphenyl itself would not possess a racemic modification since it is a symmetrical molecule, a synthesis route developed for it could easily be adapted to unsymmetrical optically active terphenyls. The intended route of the synthesis is outlined in Figure 15.

The bimolecular reduction of acetomesitylene in the second step was attempted photochemically and electrolytically with no success. It was accomplished by aluminum amalgam in ethanol-benzene solution but with the accompaniment of large amounts of by-products. The product mixture contained the meso and dl forms of 2,3-dimesityl-2,3-butanediol, the cis and trans forms of 2,3-dimesityl-2,3-epoxybutane, and methyl mesityl carbinol.

It is odd that from the reduction of acetophenone by aluminum amalgam under the same conditions, only one product, a glycol, was reported (35).

Generally a good bit of unreacted acetomesitylene was present in the product, often in large enough amounts to render the whole reaction mixture an oil. Separation of the acetomesitylene could be

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(35) K. Sisido and H. Nozaki, J. Am. Chem. Soc., 70, 777 (1948).

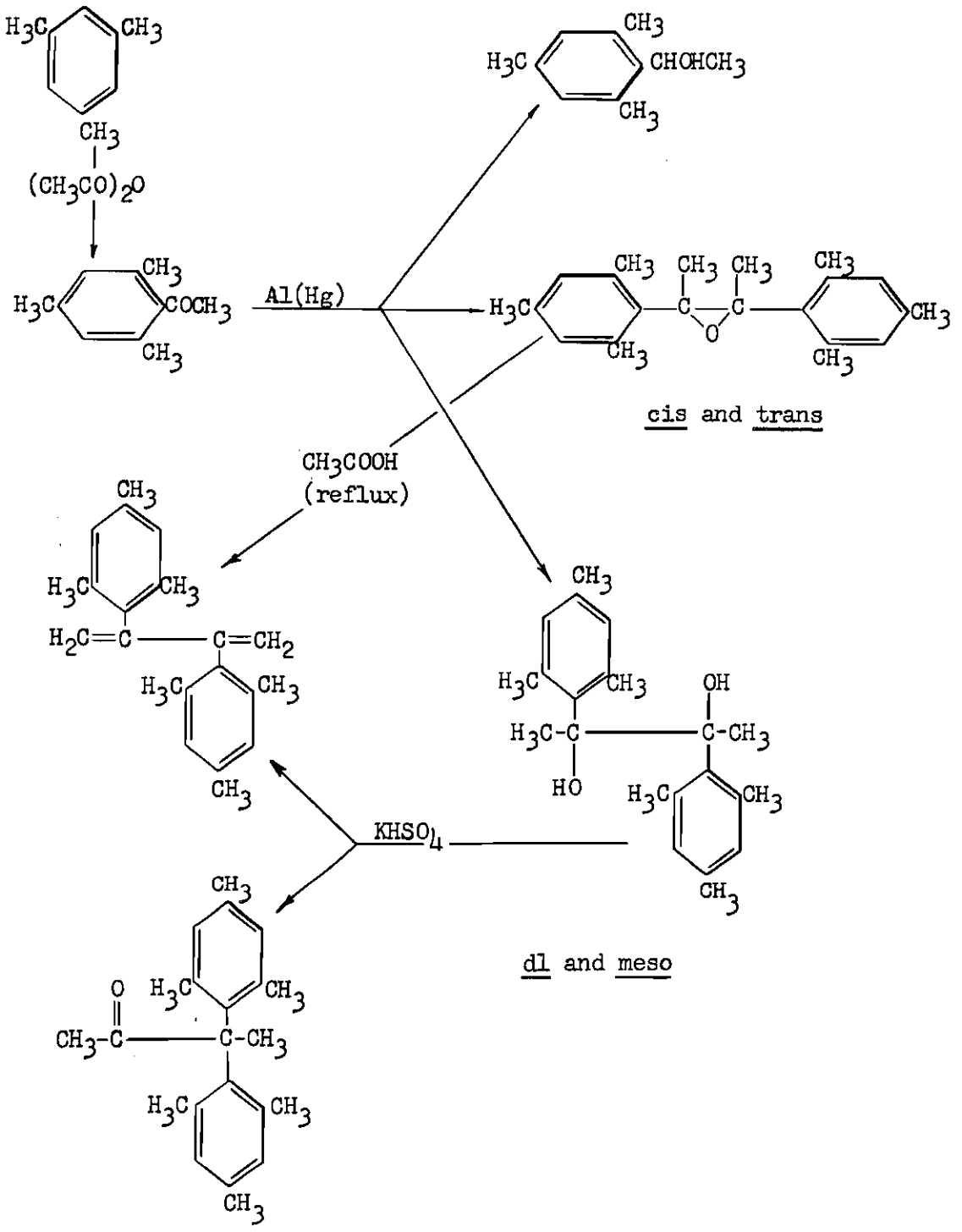

Figure 15. Intermediates in the Route to 2,2",4,4",6,6"-Hexamethyl-o-terphenyl-4',5'-dicarboxylic Acid.

accomplished by vacuum distillation at 100°C. under 1 mm. pressure or by steam distillation from neutral solution. By both methods the aceto-mesitylene carried with it most of the methyl mesityl carbinol that was present.

The separation of the other products of the reaction could be effected satisfactorily only by chromatography. Treatment of the mixture with chloroform or carbon tetrachloride achieved a partial separation since the glycols only slowly dissolved, and the dl form of the glycol was found to be more soluble in ethanol than the meso form. None the less, fractional crystallization at best allowed only partial success in separation. The oxides were particularly hard to separate by crystallization.

The formation of oxides as a by-product from the bimolecular reduction of aryl (and sometimes alkyl-aryl) ketones is not unusual (36)(37). In the present work the proportion of oxide to glycol in the product varied greatly and seemed to depend on the concentration of the acid used to decompose the pinacol complex at the end of the aluminum amalgam reduction. Thorner and Zincke (38) reduced benzophenone with zinc and hydrochloric acid and obtained only diphenylstilbene oxide, which they asserted resulted from the action of the acid on the glycol which had first formed.

The compounds named as oxides were so assigned on the basis of their elemental analyses, molecular weights, and infrared spectra. The

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(36) W. Thorner, Ann., 189, 104 (1877).

(37) F. H. Tendick, U. S. Patent 2,393,129 (January 15, 1946).

(38) W. Thorner and T. Zincke, Ber., 11, 65 (1878).

suspected cis oxide melted at 119.5°-120.5°C., and the suspected trans isomer melted at 92°-93°C. The spectra of these two compounds were strikingly similar. There was but one slight difference. The spectrum of the higher melting oxide had a single strong, wide band at 9.20 microns. The corresponding band in the spectrum of the lower melting oxide was a doublet. The spectra were in reasonable harmony with the proposed oxide structure, but inconsistent with spectra expected of ketones, alcohols and compounds containing carbon-carbon unsaturation which are other possible products from this reaction.

Qualitative tests for ketones and unsaturated compounds were performed. All of the results were negative. Even if the compounds had been ketones or olefins, steric hindrance would probably have prevented positive results. Therefore, no dependence was placed on these negative results.

Dioxanes also could be formed from this bimolecular reduction. The possible dioxanes would analyze the same as the oxides and probably have very similar spectra. However, the molecular weight of the dioxanes would be 616, while that of the oxides would be 308, half that of the dioxanes. The determined molecular weights of 268 and 279 (Rast method) for the two compounds excluded the possibility of their being dioxanes.

The compound assigned as meso-2,3-dimesityl-2,3-butanediol was a clear crystalline material which melted at 172°-173°C. The infrared spectrum of this compound was in complete harmony with one expected for a glycol, and its elemental analysis checked closely with that calculated for this glycol. This material reacted with periodic acid to yield

acetomesitylene, the expected scission product. Further, it could be dehydrated by potassium bisulfate to yield 2,3-dimesityl-1,3-butadiene. A by-product of the dehydration was 3,3-dimesitylbutanone-2. This ketone was doubtlessly formed by the pinacol rearrangement of meso-2,3-dimesityl-2,3-butanediol. An attempted dehydration of the diol by acetyl bromide failed to yield any pure products.

The instability to heat of this glycol is in agreement with behavior reported for other aryl glycols. Thorner and Zincke (39) heated benzopinacol just above its melting point whereupon the glycol decomposed to benzophenone and benzhydrol. When meso-2,3-dimesityl-2,3-butanediol was heated just above its melting point for an hour, it decomposed to a white solid and a liquid whose refractive index checked with that of acetomesitylene.

The spectrum of the fourth compound isolated, which melted at 155°-156°C., was that of a typical alcohol. This evidence, coupled with the reasonable agreement of its carbon and hydrogen analysis with the calculated values for 2,3-dimesityl-2,3-butanediol, and its cleavage to acetomesitylene by periodic acid, led to its identification as one of the 2,3-dimesityl-2,3-butanediol isomers. It was suspected of being the dl modification, therefore an attempt was made to resolve the compound.

The only recorded clear-cut resolution of a racemic alcohol by crystallization is that of dl-isohydrobenzoin, a glycol similar to

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(39) W. Thorner and T. Zincke, Ber., 10, 1473 (1877).

2,3-dimesityl-2,3-butanediol. Read and coworkers (40) reported that the crystallization of dl-isohydrobenzoin from ethyl acetate or chloroform yielded hemimorphic crystals. Solutions of single crystals that they obtained were found to be optically active. It was therefore decided to attempt such a resolution with 2,3-dimesityl-2,3-butanediol. Large crystals of 2,3-dimesityl-2,3-butanediol were obtained by slow crystallization from ether, ethanol, ethyl acetate, and chloroform. The clear crystals obtained from ethyl acetate and chloroform were particularly well formed. Several single crystals obtained from each of these solutions were examined for optical rotation but none showed any noticeable activity. The same slow crystallization was then tried with the higher melting glycol, but none of the crystals examined showed any optical activity.

The lower melting glycol was not investigated as closely as the glycol which melted at 172°-173°C., mainly because it was formed in only small amounts and purified with difficulty. Furthermore, its melting behavior was peculiar. If the melting point was taken slowly, the diol melted at 144.5°-145.5°C. If it was taken rapidly, the compound melted at 155°-156°C.

Two different attempts were made to determine unequivocally the identity and steric configuration of the two oxides and the two diols. Both attempts were based on the known direction of oxide ring opening. The opening of a variety of oxides of open chain olefins has been shown to proceed with Walden inversion. Thus, optically active trans-2,3-

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(40) J. Read, I. G. M. Campbell, and T. V. Barker, J. Chem. Soc., 1929, 2305.

epoxybutane is known to give optically inactive meso-2,3-butanediol. On the other hand, cis-2,3-epoxybutane gives rise to dl-2,3-butanediol (41).

The first attempt was an acid catalyzed hydrolysis performed on the suspected trans-2,3-dimesityl-2,3-epoxybutane. The resulting product should have been meso-2,3-dimesityl-2,3-butanediol. However, the ring failed to open. This was probably due to the insolubility of the oxide in the predominantly aqueous medium and to the steric hindering effect of the bulky mesityl groups.

An attempt was then made to form diacetate esters from both the oxides and the diols. One oxide and one diol would give the same diacetate. By determining which oxide and which diol gave the same diacetate it would be possible to prove the relative steric configuration of these four compounds. If one diol could then be resolved, that would be information enough to assign unambiguously the identity of all four compounds.

The suspected trans oxide was reacted with acetic anhydride in order to form its diacetate. Extensive charring occurred and no pure product was obtained. Acetyl chloride and dimethylaniline was then reacted with the suspected meso diol. This attempt failed to yield a diacetate as did a second attempt in which sulfuric acid was used as the catalyst. One attempt, already mentioned, was made to resolve the glycols without success. In view of these results, the identification work was halted and no further resolution of the diols was attempted.

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(41) C. E. Wilson and H. J. Lucas, J. Am. Chem. Soc., 58, 2396 (1936).

Configurations of these compounds then had to be tentatively assigned on the basis of melting points of similar molecules. An examination of the melting points of several substituted 2,3-butanediols revealed that the meso isomer was the higher melting compound. Likewise, the higher melting isomer of several checked 2,3-epoxybutanes was the cis form.

The fifth product obtained from the reduction of acetomesitylene was methyl mesityl carbinol. This alcohol was identified both by elemental analysis and by the correspondence of its melting point with the literature value.

3,3-Dimesitylbutanone-2, the by-product from the potassium bisulfate dehydration of meso-2,3-dimesityl-2,3-butanediol, was assigned its structure on the basis of its elemental analysis, infrared spectrum, and the results of the iodoform test performed on it. When this compound was treated with sodium hypoiodite it yielded no iodoform but formed yellow crystals which melted at 132°-136°C. It is known that methyl ketones containing bulky groups attached to the carbonyl carbon atom fail to give a positive iodoform test. But it is also known that they can react to give a product other than iodoform (42).

While acetomesitylene failed to yield iodoform when treated with sodium hypoiodite, Fuson and Bull (42) have claimed the isolation of α,α-diiodoacetomesitylene from the reaction.

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(42) R. C. Fuson and B. A. Bull, Chem. Revs., 15, 275 (1934).

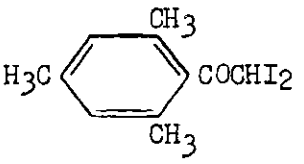

Figure 16. α,α-Diiodoacetomesitylene

A positive halogen test from a sodium fusion performed on the yellow crystals and the slow development of a purple color in the crystals upon standing in light, proved the presence of iodine in the molecule. Therefore, it is postulated that the result of the iodoform reaction was a partially iodinated methyl ketone. This would not have been possible if the ketone were the isomeric ketone, the other pinacol rearrangement product, shown in Figure 17.

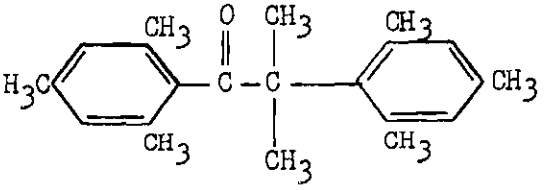

Figure 17. 1,2-Dimesityl-2-methylpropanone-1

3,3-Dimesitylbutanone-2 failed to yield an oxime upon being refluxed with hydroxylamine hydrochloride and pyridine. But since acetomesitylene itself fails to form an oxime it is not surprising that this more hindered ketone failed to oximate as well.

A single attempt to condense 2,3-dimesityl-1,3-butadiene with maleic anhydride under mild conditions failed and the route to 2,2",4-

4",6,6"-hexamethyl-o-terphenyl-4',5'-dicarboxylic acid was stopped at this point.

CHAPTER III

EXPERIMENTAL PROCEDURES

Attempts to Prepare ortho- and meta-Terphenyls with Restricted Rotation Utilizing Ullmann Reactions

Attempted Preparation of Trimethyl 2,2"-Dinitro-o-terphenyl-3'6,6"-tricarboxylate

Preparation of Anhydro-2-hydroxymercuri-3-nitrobenzoic Acid.--This material was prepared by the method of Whitmore, Culhane, and Neher (43) by which mercuric acetate is reacted with the disodium salt of 3-nitrophthalic acid. The product was not weighed but was used moist for the preparation of 2-bromo-3-nitrobenzoic acid.

Preparation of 2-Bromo-3-nitrobenzoic Acid.--Bromination of anhydro-2-hydroxymercuri-3-nitrobenzoic acid as recommended by Culhane (44) afforded the compound in 58.5 per cent yield.

Preparation of Methyl 2-Bromo-3-nitrobenzoate.--2-Bromo-3-nitrobenzoic acid dissolved in methanol saturated with hydrogen chloride was esterified, according to the directions of Ingersoll and Little (45) in 96 per cent yield.

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(43) F. C. Whitmore, P. J. Culhane, and H. T. Neher, Organic Syntheses, Coll. Vol. I, John Wiley and Sons, Inc., New York, N.Y., 1956, p. 56.

(44) P. J. Culhane, Organic Syntheses, Coll. Vol. I, John Wiley and Sons, Inc., New York, N.Y., 1956, p. 125.

(45) A. W. Ingersoll and J. R. Little, J. Am. Chem. Soc., 56, 2123 (1934).

Preparation of Dimethyl 6,6'-Dinitrodiphenate.--The Ullmann reaction coupling methyl 2-bromo-3-nitrobenzoate was carried out two ways: without use of solvent and with the use of dimethylformamide as solvent. For both methods the activation of the copper bronze was carried out precisely as described by Fuson and Cleveland (46), whose directions are based on the original method of Kleiderer and Adams (47). The dimethylformamide used was duPont technical grade and was not given any special drying treatment.

Ullmann Reaction in Absence of Solvent.--By using the method of Ingersoll and Little (45) a 72 per cent average yield of three attempts was realized. The melting point of 128°-129°C. agreed with that previously reported (45).

Ullmann Reaction with Dimethylformamide as Solvent.--This method was adapted from the procedure described by Kornblum and Kendall (7) for the preparation of 2,2'-dimethoxy-6,6'-dinitrobiphenyl.

A mixture of 18.0 g. of methyl 2-bromo-3-nitrobenzoate and 100 ml. of dimethylformamide was placed in a 200 ml. three-necked flask equipped with a reflux condenser and a stirrer. When the temperature was approximately five degrees below the reflux temperature, 20.0 g. of activated copper powder was quickly added. The exothermic reaction rapidly brought the mixture to reflux. The refluxing was continued for four hours. A second 20.0 g. of copper powder was added and the re-

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(46) R. C. Fuson and E. A. Cleveland, Organic Syntheses, Coll. Vol. III, John Wiley and Sons, Inc., New York, N.Y., 1956, p. 339.

(47) E. C. Kleiderer and R. Adams, J. Am. Chem. Soc., 55, 4219 (1933).

action mixture was maintained at reflux temperature for another four hours. After cooling, the mixture was poured into several liters of water and the solid which formed was removed by filtration. Using a Soxhlet extractor, the solid was extracted with acetone until the extracting solvent became nearly colorless. The acetone extract was concentrated to a small volume and the yellow crystals which separated were filtered. After recrystallization from methanol, 7.0 g. of yellow crystals melting at 128°-129°C. were obtained for a 56 per cent yield.

Attempted Preparation of Dimethyl 6-Amino-6'-nitrodiphenate by the Reduction of Dimethyl 6,6'-Dinitrodiphenate.--

Using Sodium Polysulfide.--A compound was obtained which analyzed for nitrogen close to the value calculated for the cyclic azo derivative of dimethyl 6,6'-dinitrodiphenate solvated with two moles of ethanol. The reduction method employed was that which Purdie (20) used for the preparation of 2-amino-2'-nitrobiphenyl.

A solution of 3.0 g. of dimethyl 6,6'-dinitrodiphenate in 25 ml. of 95 per cent ethanol was put in a 100 ml. round-bottomed flask fitted with a reflux condenser. When the solution had been brought to a boil, a hot solution of 0.35 g. of sulfur and 1.8 g. of crystallized sodium sulfide in 6.0 ml. of water was added dropwise. After three hours of refluxing, the reaction gave a negative test for sulfide ion with lead acetate paper. The solution was then allowed to cool and stand overnight. In the morning the contents of the flask was poured into two to three times its volume of water and the mixture was extracted with several 35 ml. portions of ether. The extract was dried for several days over potassium hydroxide pellets, the pellets being replaced by

clean pellets when they became dirty. Evaporation of the ether left a yellow residue which was washed quickly with carbon disulfide to remove any sulfur. There remained 0.1 g. of a clean yellow material which melted at 137°-138.5°C. Recrystallization from a small amount of 95 per cent ethanol raised the melting point to 138.5°-139.5°C.

Anal. Calc. for $C_{20}H_{24}N_2O_6$: N, 7.17

Found: N, 7.18

From an attempt at diazotization followed by addition of potassium iodide, only starting material was recovered.

Using Platinum Oxide and Hydrogen.--A material appearing to be 6,6'-diaminodiphenic acid dilactam was obtained from this reduction.

A mixture of 1.0 g. of dimethyl 6,6'-dinitrodiphenate, 0.01 g. of platinum oxide catalyst, and 100 ml. of benzene was placed in a hydrogenation shaking apparatus. At room temperature and an initial pressure of 34.50 lbs., shaking was begun. After three hours no significant further drop in pressure was noted so the hydrogenation was stopped.

The spent platinum was filtered off and the benzene was evaporated. An acetone wash of the residue removed some yellow colored material and left 0.3 g. of a white residue. This solid was not appreciably soluble in the usual organic solvents or in dilute acids or bases. It was soluble in concentrated sulfuric acid. This acid solution fluoresced deep blue under ultraviolet light. Tiny, greenish-yellow, crystalline needles could be precipitated by cautious dilution of the solution with a small amount of water. These needles could be further purified by sublimation.

Attempts to diazotize this material failed. The solid did not melt by 300°C. and an ignition test showed that it burned, without melting, and left no residue. The needles resisted acetylation by boiling acetic anhydride. Since it was not possible to compare the starting material and the acetylation residue by their melting points, an infrared spectrum of each was made. The two proved to be identical.

A comparison of the infrared spectrum of this white solid and the spectra of the white solids obtained from the other methods of reducing dimethyl 6,6'-dinitrodiphenate described below, proved this material to be different from the others.

Anal. Calc. for $C_{14}H_8N_2O_2$: N, 11.86

Found: N, 11.78

Using Zinc and Ammonium Chloride.--This reduction yielded 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene and 1,10-dicarbomethoxybenzo(c)cinnoline-5-oxide.

A solution of 1.0 g. of dimethyl 6,6'-dinitrodiphenate in 25 ml. of methanol was placed in a 100 ml. three-necked flask fitted with a stirrer and a reflux condenser. The solution was heated to 60°-65°C. and 0.5 g. of ammonium chloride in 10 ml. of water was added. This caused some of the ester to come out of solution so a little acetone was added to complete solution. Zinc dust was slowly added by spatula-end portions until no further color change was detected and zinc metal appeared to be suspended in the solution. The temperature was then kept at 60°-65°C. for about two hours. At the end of this time the reaction sludge was filtered off and washed with warm acetone. The filtrate and

washings, which contained 1,10-dicarbomethoxybenzo(c)cinnoline-5-oxide, were reserved for later treatment.

The moist sludge was now treated with dilute hydrochloric acid. The zinc hydroxide and the excess zinc dissolved, leaving behind 0.45 g. of a pale cream colored residue, 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene. This solid was not appreciably soluble in hot water, acetone, hot 95 per cent ethanol or other usual organic solvents. Hot dimethylformamide and hot methyl cellosolve did dissolve the solid but the material reprecipitated by dilution with water was not crystalline and was hard to filter. It was only slightly soluble in dilute acids as well as concentrated hydrochloric acid but was soluble in 85 per cent phosphoric acid and concentrated sulfuric acid. Hot glacial acetic acid did not dissolve the solid but turned it red and flocculent. It could not be steam distilled from either acidic, basic, or neutral media. Strong basic reagents in general would, at least, partially dissolve the solid, imparting a green color to the remaining solid and to the solution.

The solid did not melt by 360°C., although by this temperature it was somewhat charred. An ignition test then showed that it burned, but did not melt, and left no residue. The material was not diazotizable.

Anal. Calc. for $C_{14}H_8N_2O_4$: C, 62.69; H, 3.00; N, 10.44

Found: C, 62.64; H, 3.05; N, 10.80

5,10-Dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene was acetylated by boiling acetic anhydride. The infrared spectrum of

this material was in harmony with one expected of such an acetylated structure.

Anal. Calc. for $C_{18}H_{12}N_2O_6$: C, 61.36; H, 3.43; N, 7.95

Found: C, 60.79; H, 3.40; N, 7.92

The filtrate and washings of the reaction sludge, which had been set aside earlier, contained 1,10-dicarbomethoxybenzo(c)cinnoline-5-oxide. The combined filtrate and washings was evaporated to about half its volume. An equal amount of water was added and the solution was chilled. The small amount of yellow crystals which slowly separated were removed by filtration and dried. Recrystallization from 95 per cent ethanol yielded 0.02 g. of crystals melting at 184°-185°C. These crystals were soluble in acetone, benzene, and hot 95 per cent ethanol, fairly soluble in ether, and only very slightly soluble in ligroin, and hot water. Concentrated hydrochloric acid dissolved the yellow crystals and upon concentrating the volume, white fibrous crystals separated. These white crystals had the same melting point as the yellow crystals, 184°-185°C. The yellow crystals were not diazotizable nor could they be acetylated by boiling acetic anhydride, material melting at 184°-185°C. being recovered in both cases. The infrared spectrum of this material was taken.

Anal. Calc. for $C_{16}H_{12}N_2O_5$: N, 8.97

Found: N, 9.14

Using Tin and Hydrochloric Acid.--A mixture of 1.0 g. of dimethyl 6,6'-dinitrodiphenate, 3.0 g. of mossy tin, and 35 ml. of 1:1 hydrochloric acid was placed in a 100 ml. flask. A condenser was attached and the mixture was heated until most of the tin was dissolved. The

stannous ions were removed by precipitating stannous sulfide with hydrogen sulfide. After the excess hydrogen sulfide was expelled, the solution was made basic with ammonia whereupon 0.55 g. of a white solid precipitated. This solid was not appreciably soluble in any of the usual organic solvents, and did not melt by 360°C. An ignition test then showed that it would not melt but burned to leave a slight white residue which spectroscopic analysis proved to be tin oxide. Further tests upon this solid gave results identical to those of the tests carried out upon the white solid obtained from the zinc and ammonium chloride reduction of dimethyl 6,6'-dinitrodiphenate, described above.

The infrared spectrum of this white solid was identical to that of 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene except for a few very weak bands. Further, when this solid was treated with boiling acetic anhydride the product possessed an infrared spectrum identical to that of acetylated 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene. The action of sodium hydroxide on 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene was partially investigated. A mixture of 0.25 g. of the white solid and 50 ml. of a 50 per cent aqueous ethanol solution containing 2.0 g. of sodium hydroxide was refluxed for four hours. The white solid was converted to a green solid which partially dissolved to give a green solution. The mixture was filtered hot. Upon cooling, the filtrate deposited a small amount of brilliant yellow-green crystals and dilution with water caused a further amount to separate. Acidification of the filtrate precipitated a flocculent white solid with a red tinge. Hot acetic anhydride dissolved the white portion and left a red solid. The acetylated white portion had an

infrared spectrum which was identical with acetylated 5,10-dioxo-4,5,-9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene.

The green residue from the filtered basic solution could be washed with water to give a clear basic solution from which a white precipitate was obtained upon acidification. This white precipitate had an infrared spectrum very similar to that of 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene.

Using Sodium Sulfide and Sodium Bicarbonate.--A 100 ml. three-necked flask was fitted with a reflux condenser, a stirrer, and a dropping funnel. A solution of 4.14 g. of dimethyl 6,6'-dinitrodiphenate in 40 ml. of methanol was placed in the flask and brought to gentle reflux. A mixture of 4.0 g. of sodium sulfide nonahydrate and 1.25 g. of sodium bicarbonate dissolved in 10 ml. of water was then added dropwise. After one and one-half hours the yellow solution had turned orange-brown and a test for sulfide ion with ferrous sulfate paper was negative. The contents of the flask were then poured into about 200 g. of ice and water. The resulting yellow precipitate was removed by filtration and washed with water. The filtrate was reserved for later treatment.

Hot 1:1 hydrochloric acid was used to leach the yellow solid, but upon neutralization of the extract only a very small amount of a white flocculent solid precipitated. An acetone wash of the remaining yellow solid removed the yellow coloring matter and left behind 0.28 g. of a nearly white (greenish tinge) solid.

The filtrate, reserved from the filtration of the yellow solid, was made acidic. The acidified filtrate yielded 0.8 g. of 6,6'-dinitro-

diphenic acid, resulting from saponification of the ester during the reaction, and 0.11 g. of a dull white solid shown by its infrared spectrum to be identical with the greenish white solid above. A close comparison of the properties and infrared spectrum of this compound was made with that of 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene, obtained from the zinc and ammonium chloride reduction method described above. Since the properties and spectra of the two compounds corresponded exactly, they were assumed to be identical and an analysis of this material was omitted.

Attempted Preparation of Dimethyl 2,2',2",5'-Tetranitro-m-terphenyl-6,6"-dicarboxylate

Preparation of 2,6-Dibromo-p-nitroaniline.--This compound was prepared by brominating p-nitroaniline according to the method of Holleman (26), in 97.5 per cent yield. The melting point of 202°-203°C. was in close agreement with the literature values. However, sublimation or several recrystallizations from ethanol raised the melting point to 206°-207°C.

Preparation of 2,6-Dibromo-1,4-dinitrobenzene.--The following preparation of this compound was based on the work of Emmons (27).

A mixture of 23.6 g. of 2,6-dibromo-p-nitroaniline and 100 ml. of trifluoroacetic acid was put in a 300 ml. three-necked flask. The flask was fitted with a stirrer, a dropping funnel, and a thermometer mounted in a cut away cork. The assembly was then placed in a hood. By means of a heating mantle the temperature was raised to 40°-45°C., at which temperature the dropwise addition of 11.0 ml. of 90 per cent hydrogen peroxide was started. In about one minute the temperature be-

gan to climb steadily. By removing the heating mantle and intermittently cooling the flask with cold water, the temperature was held at 60°-65°C. Frothing occurred and the light yellow needles of the amine dissolved and were replaced by stubby orange needles. After the addition of the peroxide was completed, the frothing stopped and the temperature began to fall. The heating mantle was replaced and the temperature was maintained at 60°-65°C. for 15 more minutes. The flask was allowed to cool to room temperature and the contents were poured into about 300 ml. of water. After the precipitate coagulated, it was filtered and dried.

The crude product was quickly washed with small portions of cold glacial acetic acid. This effectively removed some dark tarry material from the product, leaving a clean yellow crystalline solid. However, the wash also slowly dissolved the 2,6-dibromo-1,4-dinitrobenzene which was the bulk of the yellow solid. This dissolved dinitro compound was recovered in a somewhat impure state by diluting the acetic acid wash with water, filtering off the solid, and recrystallizing from 95 per cent ethanol using a liberal amount of decolorizing charcoal.

Purification by chromatography led to a purer product. The crude material was dissolved in the least amount of chloroform and absorbed on a silicic acid-chloroform column. Only a short column, five or six centimeters in height, was needed because the impurities stuck fast at the top of the column while the dinitro compound was easily eluted with chloroform. The material recovered from evaporation of the chloroform was recrystallized once from 95 per cent ethanol.

The clean yellow solid left from the cold glacial acetic acid wash of the tarry product was 2,6-dibromo-1,4-dinitrobenzene containing some unreacted starting material. The dinitro compound was separated by allowing the mixture to stand in glacial acetic acid at room temperature until the yellow flakes of the dinitro compound dissolved and left behind the fine crystals of the amine. The amine was removed by filtration. By diluting the acetic acid filtrate with water, the dinitro compound was recovered. Recrystallization was from 95 per cent ethanol. The melting point was 129°-130°C. in agreement with the literature (48). The combined weight of the various portions of 2,6-dibromo-1,4-dinitrobenzene was 18.4 g. for a 70 per cent yield.

The Ullmann Reaction between 2,6-Dibromo-1,4-dinitrobenzene and Methyl 2-Bromo-3-nitrobenzoate.--A thermometer and a test tube 2.5 cm. in diameter and 15 cm. in length were both immersed in an oil bath and clamped in position. The bath was heated to 180°C. and 3.6 g. of 2,6-dibromo-1,4-dinitrobenzene and 11.44 g. of methyl 2-bromo-3-nitrobenzoate were added to the test tube. The melt was mixed thoroughly. Then 8.0 g. of activated copper powder (46) was gradually added in spatula-end portions with stirring after each addition. The temperature rose steadily to 210°-220°C. where it was held until the end of the copper addition. This took about 30 minutes. The temperature was then maintained at 220°-225°C. for 30 minutes longer. After the test tube was cooled to room temperature it was broken, the reaction mass removed and extracted with acetone in a Soxhlet extractor. The acetone was evaporated and the reaction mixture was dried. The weight of the mixture was 8.5 g.

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(48) G. Korner and A. Contardi, Atti accad. Lincei, 22, ii, 631 (1913).

To separate the reaction products, fractional crystallization from 95 per cent ethanol was tried first. The first crop of crystals was 1.5 g. of reasonably pure dimethyl 6,6'-dinitrodiphenate, but thereafter no pure fraction could be obtained.

The ethanol solvent was then evaporated and the residue was dried. The mixture was taken up in the least amount of chloroform and put on a column of silicic acid suspended in chloroform 19.4 cm. high and 4.3 cm. in diameter. Elution was by chloroform. Three very thin yellow bands developed close to the moving front, but in back of these the whole column was dark greenish yellow with no visible bands. The three bands were removed and the solids obtained from them were recrystallized from 95 per cent ethanol.

Band #1 contained 0.1 g. of methyl 2-bromo-3-nitrobenzoate.

Band #2 contained 0.05 g. of methyl 2-bromo-3-nitrobenzoate and 0.2 g. of dimethyl 6,6'-dinitrodiphenate.

Band #3 contained 0.7 g. of dimethyl 6,6'-dinitrodiphenate.

The rest of the material was stripped from the column with a 1:1 methanol-chloroform mixture and dried. The dry samples was then vacuum sublimed at 70°C. and 2 mm. pressure, whereupon 0.1 g. of methyl 2-bromo-3-nitrobenzoate was obtained. Increasing the temperature of the sublimation failed to yield any pure component. The separation attempt was then abandoned.

Attempted Preparation of Dimethyl 2,2"-Dinitro-o-terphenyl-6,6"-dicarboxylate

Preparation of o-Iodonitrobenzene.--The method of Baeyer (49), by which o-nitroaniline is diazotized and treated with potassium iodide, was used to prepare this compound. The material melted at 53°C. and the yield was nearly quantitative.

Preparation of o-Iodoaniline.--Baeyer's method (49) for the preparation of this compound by reducing o-iodonitrobenzene with stannous chloride afforded material melting at 60°-61°C. in 85 per cent yield. The melting point agreed with the literature.

Preparation of o-Diiodobenzene.--This compound was prepared by the diazotization method of Korner and Wender (50). The yield of material, boiling at 109°C at 3.0 mm. pressure, was 35 per cent of the theoretical.

The Ullmann Reaction between o-Diiodobenzene and Methyl 2-Bromo-3-nitrobenzoate.--

With Dimethylformamide as Solvent.--A mixture of 5.0 g. of o-diiodobenzene and 5.0 g. of methyl 2-bromo-3-nitrobenzoate was placed in a 100 ml. three-necked flask equipped with a stirrer and reflux condenser. To this mixture was added 35 ml. of dimethylformamide and the whole brought to reflux. To the refluxing solution 7.5 g. of activated copper powder (46) was added in small portions. The solution turned green immediately but gradually changed to an orange-brown.

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(49) A. Baeyer, Ber., 38, 2759 (1905).

(50) E. G. Korner and V. Wender, Gazz. chem. ital., 17, 486 (1887).

After the addition was completed, the solution was refluxed for two hours. At the end of this time 7.5 g. more copper powder was added and refluxing was continued for three additional hours. The flask was allowed to cool and the contents were poured into 800 ml. of water. When the precipitate had coagulated it was filtered off and dried. The precipitate was then extracted several times with hot 95 per cent ethanol. Several crops of crystals were obtained by successive evaporation and chilling of the alcohol leach. In this way 1.1 g. of dimethyl 6,6'-dinitrodiphenate and a very small amount of unreacted methyl 2-bromo-3-nitrobenzoate were recovered but none of the desired product was found.

With No Solvent.--In a 100 ml. flask were placed 7.0 g. of o-diiodobenzene and 7.0 g. of methyl 2-bromo-3-nitrobenzoate. The flask was heated by a heating mantle to 200°C. and, after thoroughly stirring the melt, a spatula-end of activated copper powder (46) was added. The temperature rose very rapidly to over 220°C. The flask was cooled somewhat and the temperature was held around 200°C. By the time 6.0 g. of copper had been added, the melt was so thick and gummy that stirring was impossible. The reaction mixture was allowed to cool and was then extracted with acetone. Successive evaporations of the acetone yielded 2.2 g. of dimethyl 6,6'-dinitrodiphenate, 0.4 g. of methyl 2-bromo-3-nitrobenzoate, and a small quantity of o-diiodobenzene. None of the desired o-terphenyl was found.

Attempted Preparation of 3',6,6"-Trimethyl-2,2"-dinitro-o-terphenyl

Preparation of 2-Methyl-6-nitroaniline.--The method of nitrating o-

toluidine suggested by Howard (51) afforded this material in 55 per cent yield. When the crude product was purified by steam distillation, a material of satisfactory yield and purity was obtained by collecting only 24 liters of distillate rather than the 36 liters recommended.

Preparation of 2-Iodo-3-nitrotoluene.--The method of Wittig and Stichnoth (52) was modified to prepare this compound.

In a two liter three-necked flask fitted with a reflux condenser, a stirrer, and a dropping funnel, was placed 60 g. of 2-methyl-6-nitroaniline. A thermometer was suspended into the flask through the reflux condenser. To the flask was now added 175 ml. of concentrated hydrochloric acid. The mixture was heated with good stirring to 80°C. This temperature was maintained until the amine dissolved. Then from the dropping funnel 900 ml. of water was slowly added. When all the water had been added, the flask was cooled to 0°C. and some precipitated amine salt that had stuck to the sides of the flask was broken loose. With vigorous stirring a solution of 28.0 g. of sodium nitrite in 75 ml. of water was slowly added. The temperature was kept in the range of 0°-5°C. Stirring of the cold solution was continued after the addition of the sodium nitrite until a nearly clear solution was obtained. A solution of 100 g. of potassium iodide in 200 ml. of water was then slowly added. After allowing the reaction mixture to

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(51) J. D. Howard, Organic Syntheses, Vol. 35, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 3.

(52) G. Wittig and O. Stichnoth, Ber., 68, 928 (1935)

stand overnight at room temperature the solid was filtered off. The dark solid was washed with dilute sodium hydroxide until the iodine color was removed.

The unreacted amine was effectively removed by stirring the solid in a strong 5:1 hydrochloric acid solution until the orange flecks of the amine disappeared. The solid was filtered, washed successively with 1:1 hydrochloric acid and water, then dried. The crude iodo compound weighed 85.5 g., which was 82.9 per cent of the theoretical yield. Instead of performing a recommended steam distillation at this point, the compound was purified just as well by washing once quickly with cold 50 per cent ethanol and then recrystallizing from ethanol-water. In this way 77.7 g., or 75 per cent, of 2-iodo-3-nitrotoluene was obtained, melting at 66°-67°C. The literature value is 68°C. (52).

Preparation of 2,2'-Dimethyl-6,6'-dinitrobiphenyl.--

Ullmann Reaction with No Solvent.--This preparation was adapted from the method of Ullmann and Frentzell (53).

A 2.5 cm. by 15 cm. test tube was immersed in an oil bath held at 185°C. In the hot test tube was placed 10.0 g. of 2-iodo-3-nitrotoluene. When this had melted, small portions of activated copper powder (46) were gradually added. The melt was stirred well with a thermometer after each addition. The exothermic reaction was held in the temperature range 200°-215°C. After 10.0 g. of copper powder was added, the temperature was maintained at 200°-210°C. for an additional 45

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(53) F. Ullmann and L. Frentzell, Ber., 38, 725 (1905).

minutes. The tube was then cooled and the reaction mass was leached with three 25-30 ml. portions of hot 95 per cent ethanol. The extract was treated with charcoal and filtered. By evaporating the ethanol to about half its original volume and chilling, 2.0 g. of 2,2'-dimethyl-6,6'-dinitrobiphenyl was obtained. Subsequent reductions in volume and chilling gave additional material and brought the total weight to 3.85 g. The compound melted at 107.5°-108.5°C. Since 2-iodo-3-nitrotoluene was quickly soluble in ligroin and 2,2'-dimethyl-6,6'-dinitrobiphenyl was only slowly so, the unreacted iodo compound was removed by a trituration in ligroin of about 10-15 secs. The filtered material weighed 3.75 g. for a 72.5 per cent yield. The compound melted at 109°-109.5°C. The literature value is 111°-112°C. (53).

Ullmann Reaction with Dimethylformamide as Solvent.--A mixture of 10.0 g. of 2-iodo-3-nitrotoluene and 35 ml. of dimethylformamide was placed in a 100 ml. three-necked flask equipped with a stirrer and a reflux condenser. The mixture was brought nearly to reflux. To the solution 5.0 g. of activated copper powder (46) was added in one portion and the mixture was allowed to reflux for three hours. At the end of this time 5.0 g. more of copper powder was added and the mixture was refluxed for an additional three hours. The flask was then allowed to cool and the contents were poured into 300 ml. of water. The sludge was filtered off, dried, and extracted four times with 30-40 ml. portions of acetone. Evaporation of the acetone left a tarry solid. Some green copper salts and some tarry material were removed by stirring the crushed solid in glacial acetic acid for several minutes. The acetic acid was diluted with water to about twice its volume. This dilution

precipitated the solid but the copper salts and the tarry material remained in the 1:1 acetic acid. The solid was filtered off, washed with water and dried. A quick trituration with ligroin dissolved out and unreacted iodo compound. After removal by filtration, the remaining solid was recrystallized from 95 per cent ethanol. Several crops of crystals totaled 3.45 g. of 2,2'-dimethyl-6,6'-dinitrobiphenyl which melted at 109°-109.5°C. The yield was 66.7 per cent.

Preparation of 2,2'-Dimethyl-6-amino-6'-nitrobiphenyl.--This compound was prepared by a modification of the method used by Purdie (20) for the preparation of 2-amino-2'-nitrobiphenyl.

A mixture of 3.0 g. of 2,2'-dimethyl-6,6'-dinitrobiphenyl and 40 ml. of 95 per cent ethanol was added to a 100 ml. flask and heated to reflux. A sodium polysulfide solution was then slowly added through the condenser. This solution was prepared by heating 0.76 g. of sulfur and 3.0 g. of sodium sulfide nonahydrate in 10 ml. of water until a clear solution was obtained. After refluxing the reaction for three hours, the contents of the flask were poured into an evaporating dish and allowed to evaporate partially in a hood. About an equal volume of water was then added and the whole mixture was extracted with three 25 ml. portions of ether. The ether was washed with water and then dried over sodium hydroxide pellets. The dried ether solution was treated with a little decolorizing charcoal, filtered, and then evaporated to dryness. The oil left from the evaporation of the ether slowly solidified. This solid was treated with several portions of warm 7.0 per cent hydrochloric acid to dissolve the amine. The acid solution

was filtered and the amine was precipitated by the addition of ammonium hydroxide. The amine was filtered off and recrystallized from ethanol and water. The yield of 2,2'-dimethyl-6-amino-6'-nitrobiphenyl thus obtained was 1.39 g. or 52.5 per cent of the theoretical. The melting point was 122°-123.5°C., compared with the literature value (54) of 122°-123°C.

Preparation of 2,2'-Dimethyl-6-iodo-6'-nitrobiphenyl.--Angeletti's method (29) for the preparation of this compound was considerably altered.

In a 100 ml. Erlenmeyer flask a paste was made of 1.0 g. of 2,2'-dimethyl-6-amino-6'-nitrobiphenyl and 0.5 ml. of concentrated sulfuric acid. To the paste was slowly added 25 ml. of water, whereupon the salt dissolved. The flask was then placed in a freezing mixture. At a temperature of 0°-5°C., a solution of 0.3 g. of sodium nitrite in 3.0 ml. of water was added dropwise. After the solution was filtered to free it from a small amount of brown precipitate, 0.6 g. of potassium iodide in 10 ml. of water was added with stirring. The reaction was heated on a steam bath for 30 minutes then allowed to stand overnight. The crude iodo compound was filtered off. In one trial it was purified by steam distillation. In another trial it was purified by vacuum sublimation. In either case, crystallization from ligroin followed. Both methods yielded 0.38 g., a 26 per cent yield, of 2,2'-dimethyl-6-iodo-6'-nitrobiphenyl which melted at 128°-129°C. The literature value is 129°-130°C. (29). Since this material was only slowly

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(54) A. Angeletti and P. Guala, Gazz. chim. ital., 61, 651 (1931).

distilled by steam, purification by vacuum sublimation at 90°-95°C. and 1.0 mm. pressure was faster.

The Iodination of m-Nitroaniline

Using Two Moles of Iodine Monochloride per Mole of m-Nitroaniline.--This procedure was adapted from a method for iodinating p-nitroaniline proposed by Sandin, Drake, and Leger (55). The compounds isolated in this experiment were identified by a comparison of the melting points and other characteristics of the iodinated compounds of m-nitroaniline listed in the literature.

A mixture of 69.0 g. (0.5 mole) of m-nitroaniline and 185 ml. of glacial acetic acid was placed in a two liter three-necked flask provided with a stirrer, a reflux condenser, and a dropping funnel. The mixture was brought to a boil in order to dissolve the amine. The heat was then turned off. With rapid stirring, a mixture of 162.5 g. (1 mole) of iodine monochloride (55) in 50 ml. of glacial acetic acid was added from the dropping funnel over a half hour. After the addition was completed, the solution was refluxed for four hours, and at the end of this time, the flask was allowed to cool to room temperature. As the reaction cooled, a mass of crystals precipitated. These crystals were filtered off and the filtrate was set aside for later treatment. The crystals were washed with cold glacial acetic acid several times and then triturated in a sodium bisulfite solution until the iodine color was discharged. The crystals were filtered off again, dried, and twice

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(55) R. B. Sandin, W. V. Drake, and F. Leger, Organic Syntheses, Coll. Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1956, p. 196.

recrystallized from 95 per cent ethanol using a little decolorizing charcoal. In this way, 16.5 g. of greenish yellow crystals, 6-iodo-m-nitroaniline, was obtained. The melting point of 157°-158°C. was in fair agreement with the literature value of 160°C. (30). These crystals were only moderately soluble in chloroform but readily soluble in hot 95 per cent ethanol.

The ethanol from the crystallization was then evaporated in stages. Four crops of crystals were obtained in the hope of isolating several of the more soluble products. Finally 0.2 g. of 2,6-diiodo-m-nitroaniline, melting at 145°-146°C., was obtained. The literature value of 145.5°C. is in close agreement (30). This was the only pure diiodo product isolated by this method.

The filtrate which had been set aside was poured into 800-900 ml. of water. A large quantity of tarry sludge was formed which was not noticeably lightened in color by treatment with sodium bisulfite. The supernatant liquid was decanted and made just basic with sodium hydroxide, whereupon a light brown precipitate formed. This solid was filtered, dried, and quickly washed with chloroform. The chloroform washed away a dark oil and left a bright yellow solid. Fractional crystallization from 95 per cent ethanol effected a separation of this yellow residue into two fractions. One fraction was 0.2 g. of 4,6-diiodo-m-nitroaniline, melting at 148.5°-149°C. The other fraction was 0.9 g. of white feathery crystals. These crystals had a tendency to sublime just below their melting point of 197.5°-198.5°C. Analysis of this material found 42.8 per cent iodine.

The tarry sludge obtained by diluting the filtrate was steam distilled from a basic solution. The product was so slowly steam distilled that only 0.1 g. of solid was realized per liter of distillate. However, steam distillation readily freed the tar from most of the excess iodine. The steam distilled solid, uncrystallized, had a melting point of 134°-138°C. It was noticed during the steam distillation that the tar had become more solid. So the water was decanted and the more solid part of the tar was pressed between paper towels. In this way, most of the adhering oil was absorbed. The solid was further cleaned by taking it up in hot 95 per cent ethanol and treating the solution with decolorizing charcoal until the color was noticeably lighter. Water was then added until no more precipitate formed. The solids were filtered and dried. This material, still somewhat crude, weighed 3.9 g. Fractional crystallization from 95 per cent ethanol finally yielded two reasonably pure fractions. These were roughly equal amounts of 6-iodo-m-nitroaniline and 4,6-diiodo-m-nitroaniline, melting at 156°-157°C. and 148°-149°C., respectively.

The separation of the components of this mixture was then attempted by chromatography. The 3.9 g. mixture was leached with 25 ml. of room temperature chloroform for several hours. Only 0.88 g. of the mixture dissolved per 10 ml. of chloroform. The residue was later carefully fractionally crystallized from 95 per cent ethanol and found to consist chiefly of 4,6-diiodo-m-nitroaniline and 2,6-diiodo-m-nitroaniline. A 10 ml. portion of the chloroform extract was put on a column of silicic acid 13.0 cm. in height and 2.2 cm. in diameter suspended in chloroform.

Elution was by chloroform. The slow moving bands that developed are shown and numbered in Figure 18. Two bands were removed by elution and the chloroform was evaporated.

Band #1 yielded an orange oil which did not solidify on standing at room temperature, on chilling in an ice chest, on standing in dry ice for a day, or on chilling an ethanol solution of it in an ice chest.

Band #2 yielded an orange crystalline solid which on recrystallization from 95 per cent ethanol gave two successive crops of crystals. These were 4-iodo-m-nitroaniline melting at 140°-141°C. and a small amount of 6-iodo-m-nitroaniline melting at 156°-157°C.

Several other bands developed near the top of the column but as they neared the bottom they widened and became too diffuse for an effective cut. This chromatographic method was nearly as valuable for cleaning the product as it was in separating its components. The tar which still contaminated the mixture as it was applied to the column remained adsorbed fast to the top of the column while elution moved the other products downward.

Due to the heavy amount of tar which formed during the reaction, a determination of the product composition could be made only roughly. The combined solids that were obtained reasonably free of tar totaled 24.0 g. Of this amount, the several products isolated were found in the approximate percentages shown.

6-iodo-m-nitroaniline	70 per cent
4-iodo-m-nitroaniline	3 per cent
4,6-diiodo-m-nitroaniline	13 per cent
2,6-diiodo-m-nitroaniline	9 per cent
White crystals melting at 197.5°-198.5°C.	5 per cent

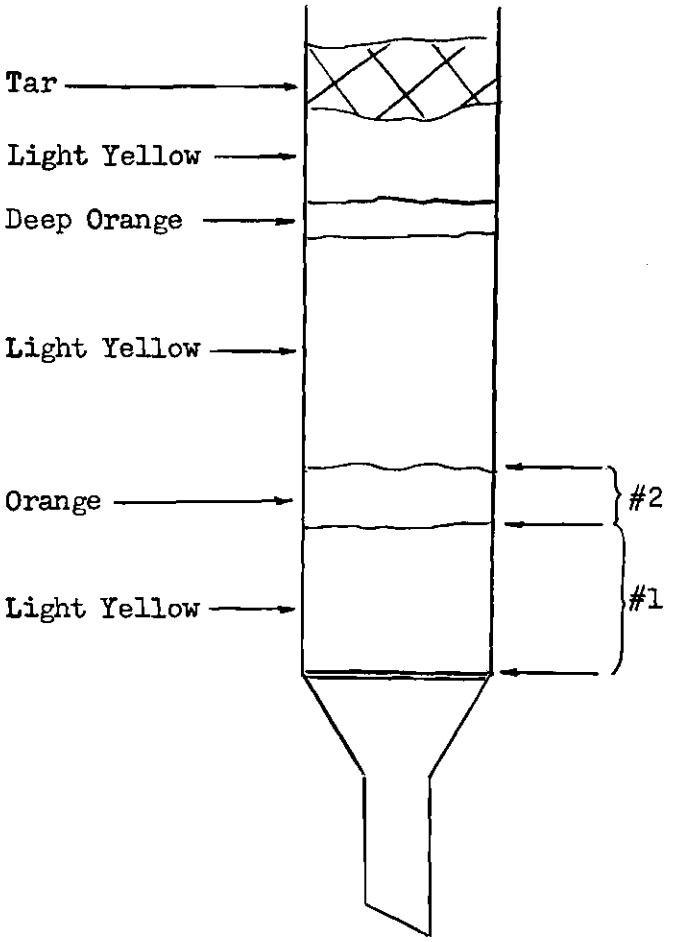

Figure 18. Chromatogram of the Products from the Iodination of m-Nitroaniline by Two Moles of Iodine Monochloride.

Using Three Moles of Iodine Monochloride per Mole of m-Nitroaniline.--This iodination was based on the method of Brenans (30).

A mixture of 40 g. (0.30 mole) of m-nitroaniline and 400 ml. of glacial acetic acid was placed in a two liter three-necked flask provided with a stirrer, a reflux condenser, and a dropping funnel. A thermometer was suspended down the condenser into the solution. The mixture was then heated to 80°C. When all the amine had dissolved, the heating mantle was turned off and a mixture of 150 g. (0.93 mole) of iodine monochloride (55) in 50 ml. of glacial acetic acid was slowly added from the dropping funnel. During the addition of the iodine monochloride the temperature remained at 80°-85°C. When all the iodine monochloride had been added, the heating mantle was removed and the flask was heated on a steam bath for two hours. The flask was then allowed to cool slowly to room temperature. After several hours, when crystals had failed to appear, the liquid was poured into one liter of water. A heavy, black, tarry sludge settled to the bottom. By decanting the supernatant liquid and neutralizing it with sodium hydroxide, 1.2 g. of a brown solid precipitated. Recrystallization twice from 95 per cent ethanol using decolorizing charcoal yielded 1.0 g. of shimmering white flakes which melted at 197.5°-198.5°C. A mixed melting point was run with this material and the white crystals melting at 197.5°-198.5°C. obtained from the iodination of m-nitroaniline with two moles of iodine monochloride. The melting point was not depressed.

In order to clean the tarry sludge of excess iodine, it was first stirred in a 10 per cent aqueous sodium bisulfite solution. The aqueous solution was unable to penetrate the large lumps of tar so this method

proved uneffective. The tar was then placed in a steam distillation apparatus and steam distilled until no more iodine appeared in the receiver or the condenser. The free iodine was thus removed quickly and efficiently.

The distillation flask was allowed to cool and the dark aqueous portion of the mixture was decanted from the heavier tar and discarded. The tar was transferred to an evaporating dish and allowed to dry under an air draft in a hood. On standing, the crude material slowly solidified. At this point its weight was 55.0 g. Much of the tar was removed by leaching the crude material with several 20 ml. portions of chloroform until the residue looked reasonably clean. The chloroform extracts were then run through a chromatographic column 2.2 cm. in diameter containing silicic acid suspended in chloroform to a height of only 4-5 cm. Most of the tar stuck to the top couple centimeters of the column while the desired products were eluted with chloroform containing 2 per cent methanol. This manuever did not completely remove the tar, but it removed enough to allow subsequent separation techniques to succeed.

In order to try to separate some of the more ethanol soluble products by fractional crystallization, several grams of the tar were triturated with 40 ml. of 95 per cent ethanol at room temperature. The triturate was decanted, treated with charcoal, and filtered. The ethanol was evaporated to about half its volume and chilled. A very small amount of dark, dirty granules were filtered off, after which the volume of the solution was reduced by about half again and chilled. The

dark feathery crystals obtained were only slowly soluble in ether, hence they could be reasonably cleaned by a wash with cold ether. The dried crystals were taken up in warm chloroform and to this solution ligroin was added until the first cloudiness appeared. The first crystals deposited were dirty yellow needles which, after several crystallizations had a melting point of 145.5°-146.5°C. This material was 2,6-diiodo-m-nitroaniline. After filtering off these crystals more ligroin was added to the chloroform whereupon a large amount of bright orange crystals precipitated. Several crystallizations from ligroin yielded crystals which melted at 139°-140°C. These crystals were 4-iodo-m-nitroaniline.

A more complete and easier method of separation was effected by chromatographic absorption on a column of silicic acid suspended in chloroform. The column was made by pouring a slurry of 25 g. of silicic acid in chloroform into a chromatographic tube 2.16 cm. in diameter, which had a removable fritted glass bottom. The amount of silicic acid used gave a packed height of 13 cm. Ten ml. of chloroform nearly saturated with the crude mixture was treated with charcoal, filtered, then put on the silicic acid column. The bands that developed upon elution with chloroform are shown in Figure 19. After band #1 had been eluted, chloroform containing two per cent methanol was used as an eluent to try to move the other slower moving bands. In the region marked #5, two orange bands originally developed. But upon elution with the methanolic chloroform, the two bands coalesced into one.

When bands #2, #3, and #4 were well developed and separated on the column no more eluent was added. The column was allowed to drain

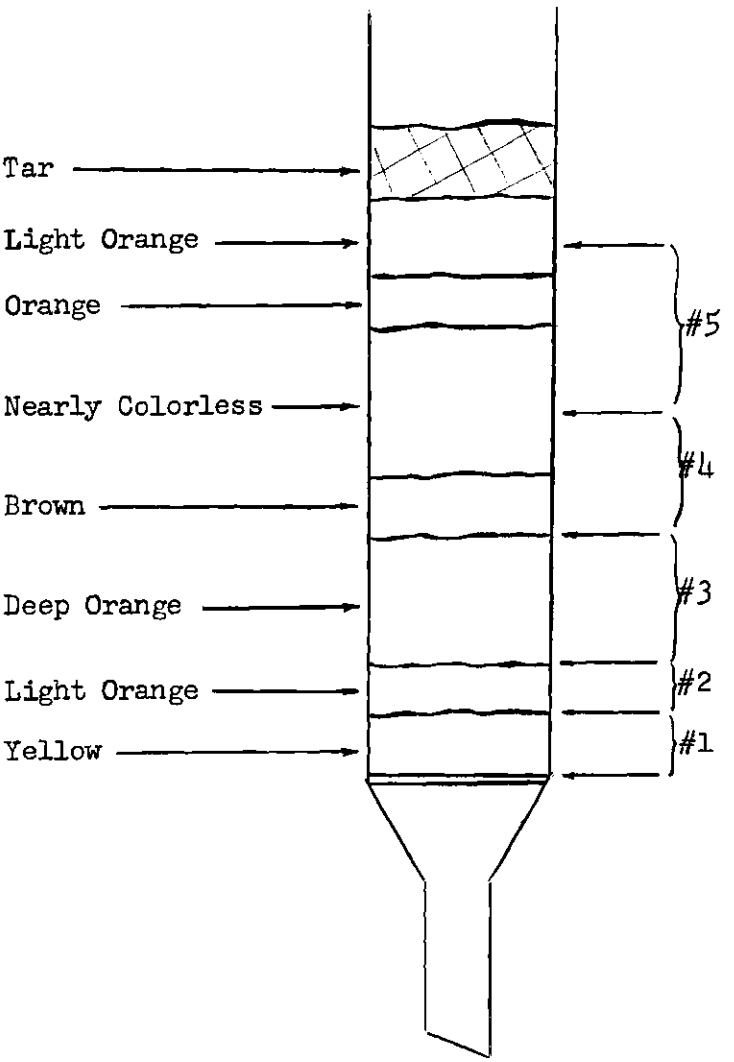

Figure 19. Chromatogram of the Products from m-Nitroaniline Iodinated by Three Moles of Iodine Monochloride.

until no more drops of chloroform fell and then was allowed to stand a half hour longer. The bottom part of the tube was then removed and the column was inverted. The bands were sectioned with a knife as the silicic acid slowly slid out. The sections of silicic acid were washed with acetone. The acetone was evaporated and the residues were recrystallized. The results are as follows:

Band #1 yielded yellow crystals. When recrystallized from ethanol and water the crystals melted at 133°-136°C. A fractional crystallization from ligroin first yielded 4,6-diiodo-m-nitroaniline melting at 148°-150°C. The more soluble fraction was 4-iodo-m-nitroaniline melting at 139°-140°C.

Band #2 contained a relatively large amount of material. Clean yellow needles of 4,6-diiodo-m-nitroaniline melting at 148°-149°C. were obtained after two crystallizations from 95 per cent ethanol. The mother liquor of these crystallizations was concentrated and chilled. A small amount of 2,6-diiodo-m-nitroaniline melting at 143°-144°C separated.

Band #3 contained only a small amount of red gum.

Band #4 contained a yellow crystalline material which was very soluble in 95 per cent ethanol. After recrystallization from ethanol and water these crystals melted at 207°-210°C. The crystals displayed a small tendency to sublime at the melting point. The material was never obtained in a large enough amount for satisfactory purification for analysis.

Band #5 contained a white amorphous solid. Upon crystallization from ethanol and water the solid melted at 233°-235°C. This material

had a tendency to sublime at its melting point. An analysis of this compound found 63.2 per cent iodine.

Of the total 40.0 g. of iodinated m-nitroaniline products collected, the composition was roughly as shown.

4,6-diiodo-m-nitroaniline	55 per cent
2,6-diiodo-m-nitroaniline	24 per cent
4-iodo-m-nitroaniline	8 per cent
White solid melting at 234°-235°C.	6 per cent
Yellow crystals melting at 207°-210°C.	4 per cent
White crystals melting at 197.5°-198.5°C.	3 per cent

Attempts to Synthesize Terphenyls by Routes Incorporating Nitrosoacylarylamines as Intermediates

Introduction.--The synthesis attempts of this section involving the coupling reaction of nitrosoacylarylamines with aromatic hydrocarbons were based on the methods devised by Heilbron, France, Hey, and their collaboratories (9)(11). The nitrosyl chloride used in these reactions was prepared according to the directions given by Bachmann and Hoffman (9).

Attempted Preparation of 2,2',2",4,4",6,6"-Heptamethyl-m-terphenyl

Preparation of 2,6-Dinitrotoluene.--

From Trinitrotoluene.--This procedure consisted of two steps. The first step was the reduction of the para nitro group of trinitrotoluene by the method of Parkes and Farthing (56). The deamination

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(56) G. D. Parkes and A. C. Farthing, J. Chem. Soc., 1948, 1275.

of the resulting para amino group was then accomplished by the method of Kornblum and Iffland (57). The yields of several runs of the reduction reaction varied from 60 to 72 per cent. The yields of the deamination reactions varied from 65 to 70 per cent.

From o-Nitrotoluene.--The method of Gibson, Duckham, and Fairbairn (58) was used to obtain a dinitro mixture from o-nitrotoluene. A 90 per cent yield was realized. The isomers were separated by the method of Parkes and Farthing (56). From 20 g. of the mixture of 2,4- and 2,6-dinitrotoluenes only 3.0 g. of pure 2,6-dinitrotoluene, melting at 65.8°-66.0°C., was obtained.

Preparation of 2,6-Diaminotoluene.--A mixture of 0.8 g. of 2,6-dinitrotoluene, 15 ml. of benzene and 0.01 g. of platinum oxide catalyst was hydrogenated at 20°C. and at a pressure of 49.50 pounds. After an induction period of about ten minutes, the pressure slowly dropped one pound. The shaking was continued, however, for three hours. At the end of this time the solution which had been deep yellow in color, was now nearly colorless. The spent catalyst was removed by filtration. The benzene was evaporated to a small volume, whereupon flaky white crystals separated. The melting point of these crystals, once washed with cold benzene, was 105.5°-106.0°C. The literature value (31) was 105°-106°C. The 70 per cent yield obtained by this method compares favorably with the yields of other methods recorded in the literature.

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(57) N. Kornblum and D. C. Iffland, J. Am. Chem. Soc., 71, 2137 (1949).

(58) W. H. Gibson, R. Duckham, and R. Fairbairn, J. Chem. Soc., 121, 270 (1922)

Preparation of 2,6-Diaminotoluene and 2,4-Diaminotoluene Mixture.--A 4.25 g. mixture of the 2,4- and 2,6-dinitrotoluene isomers obtained from the nitration of o-nitrotoluene was dissolved in 25 ml. of benzene. Then 0.06 g. of platinum oxide catalyst was added and the mixture was hydrogenated at 25°C. and 50.00 pounds pressure. The pressure slowly fell to 39.00 pounds and the temperature rose to 29.5°C. When the pressure remained steady at 39.00 pounds for 20 minutes, the shaking was stopped. The spent catalyst was filtered off, and the mixture of benzene and water of reaction was transferred to a separatory funnel and the benzene was separated. Upon evaporation of the benzene to a small volume, 2.4 g. of white crystals separated. The yield was 84 per cent. The difficult separation of this 2,4- and 2,6-diaminotoluene mixture was not attempted. Instead, the mixture was reserved for treatment with acetic anhydride in order to form the 2,4- and 2,6-diacetamidotoluene mixture which is more easily separated.

Preparation of 2,6-Diacetamidotoluene.--

From 2,6-Diaminotoluene and Acetic Anhydride.--The addition of acetic anhydride directly on solid 2,6-diaminotoluene, according to the method of Green and Lawson (31), resulted in a vigorous reaction and in the formation of the diacetyl compound. One recrystallization from a 2:3 ethanol-water mixture yielded white crystals which melted at 302°-303°C. Korolev and Rostovtzeva (59) reported the melting point (corr.) as 310°-311°C.

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(59) A. Korolev and E. Rostovtzeva, Ber., 69, 640 (1936).

From 2,6-Dinitrotoluene by Hydrogenating in the Presence of Acetic Anhydride.--A mixture of 1.0 g. of 2,6-dinitrotoluene, 15 ml. of benzene, 3.0 ml. of acetic anhydride, and 0.015 g. of platinum oxide was treated with hydrogen at 16°C. and at 35.25 pounds pressure. The mixture was shaken by a catalytic hydrogenation shaker for one hour, but no pressure drop was noticed. The apparatus was allowed to sit for two hours and the shaking was resumed. This time there was a rapid temperature rise to 23°C. and a gradual pressure drop to 33.50 pounds. By alternately shaking and cooling the apparatus, the temperature of this exothermic reaction was kept between 25°-30°C. When an hour passed with no further pressure drop, the shaking was stopped. A white solid which had separated from the solution was removed by filtration and recrystallized from a 2:3 ethanol-water mixture. The recrystallization flask was allowed to sit in an ice compartment for two days as completeness of precipitation proved to be slow. Finally, 0.5 g. of white, feathery crystals which melted at 302°-303°C. was obtained.

From a 2,4-Diaminotoluene and 2,6-Diaminotoluene Mixture and Acetic Anhydride.--A 2.5 g. mixture of 2,4-diaminotoluene and 2,6-diaminotoluene was treated slowly and cautiously with 5.0 ml. of acetic anhydride. When the vigorous reaction had subsided, the mixture was allowed to sit for 30 minutes with occasional stirring. The thick mixture was then poured into 50 ml. of water and warmed to destroy excess anhydride. The white solid which remained suspended in the solution was filtered off and dried.

The mixture of 2,4-diacetamidotoluene and 2,6-diacetamidotoluene was effectively separated by two methods. By one method, the mixture

was heated to about 300°C., whereupon 2,6-diacetamidotoluene sublimed into pure, white, fluffy crystals. The 2,4-diacetamidotoluene isomer did not sublime at all (31). The most convenient method of separation, however, was to stir the mixture in a 1:1 acetic acid-water mixture for about one minute. 2,4-Diacetamidotoluene dissolved rapidly while the 2,6-diacetamidotoluene isomer dissolved only very slowly. The desired 2,6-diacetamidotoluene was removed by filtration and recrystallized from water or from ethanol and water. In either case, the chilled solution was allowed to stand for two days to permit completion of the slow crystallization. The yield of 2,6-diacetamidotoluene, melting at 302°-303°C., was 0.5 g.

Attempted Hydrogenation of a Mixture of 2,6-Dinitrotoluene and 2,4-Dinitrotoluene in the Presence of Acetic Anhydride.--A 4.0 g. mixture of 2,4-dinitrotoluene and 2,6-dinitrotoluene, obtained from the nitration of o-nitrotoluene, was dissolved in 28.0 ml. of benzene and 10.0 ml. of acetic anhydride. After 0.06 g. of platinum oxide catalyst was added, the mixture was placed in a catalytic hydrogenation shaker. Shaking was started at 24°C. and 33.25 pounds pressure of hydrogen. Shaking was continued for three hours. During this time the temperature of the flask rose to 33°C. and the pressure dropped to 32.80 pounds. The apparatus was then dismantled and the benzene was filtered free from the spent catalyst. Most of the benzene was evaporated and the remaining acetic anhydride and benzene mixture was poured into three times its volume of water. A yellow-orange oil separated which dissolved upon warming the solution. Upon cooling the solution and allowing it to stand several hours, the oil separated again. The thick oil was rubbed

and chilled repeatedly but no crystallization could be induced.

Attempted Condensation of 2,6-Diacetamidotoluene with Mesitylene.--A 100 ml. three-necked flask, equipped with a stirrer and a thermometer, was set in an ice-water mixture. To the flask was added 1.1 g. of 2,6-diacetamidotoluene, 30.0 ml. of glacial acetic acid, 8.0 ml. of acetic anhydride, 2.0 g. of anhydrous sodium acetate, and 0.5 g. of phosphorous pentoxide. When the temperature of the mixture fell to 10°C., 3.0 ml. of acetic anhydride containing 1.5 ml. of nitrosyl chloride was added to the mixture dropwise. The color of the solution turned green with the first addition of nitrosyl chloride but gradually turned yellow. The reaction was stirred for one hour. The contents of the flask were then poured into ice water, whereupon a small amount of unreacted 2,6-diacetamidotoluene (0.05 g.) and an orange oil separated. The oil was extracted with three portions of cold mesitylene totaling 137 ml. The mesitylene extract was dried over anhydrous sodium sulfate for 24 hours. During this time the solution darkened considerably but no evolution of nitrogen was noticed. The excess mesitylene was then removed by fractionation. Evaporation of the remaining mesitylene under an air draft in a hood left a thick, intractable oil. The oil was chilled and rubbed with a stirring rod. No solidification could be induced so the oil was placed in dry ice overnight. When the flask was allowed to come to room temperature, the frozen solid thawed to an oil. The oil was then taken up in 95 per cent ethanol and allowed to stand at room temperature for several days. When no crystallization occurred, the flask was placed in an ice chest for several weeks. However, this too failed to promote crystallization. No pure product was ever isolated.

Attempted Preparation of 2,2',2",4,4',4",6,6',6"-Nonamethyl-3-nitro-m-terphenyl

Preparation of Bimesityl.--The Grignard coupling method of Moyer and Adams (8) was followed to prepare bimesityl in 16.5 per cent yield. The melting point of 101.0°-101.5°C. was the same as that recorded by Moyer and Adams.

Preparation of 3,3'-Dinitrobimesityl.--Bimesityl was dinitrated by the method of Adams and Joyce (32), as well as by a simpler method described by Powell and Johnson (33). The latter method was actually a procedure for the mononitration of mesitylene but was used with good results to dinitrate bimesityl. The yield from both methods was in the range of 65-72 per cent. The 3,3'-dinitrobimesityl obtained by the method of Adams and Joyce melted at 157°-158°C. which is somewhat lower than their literature value of 162°-163°C. The product obtained by the method of Powell and Johnson melted at 160°-161°C.

Preparation of 3-Amino-3'-nitrobimesityl.--3,3'-Dintrobimesityl was reduced by stannous chloride according to the method of Adams and Joyce (32). The yield of the resulting 3-amino-3'-nitrobimesityl was 65 per cent. Its melting point was 143°-144°C. compared with the literature value of 145°-146°C.

Preparation of 3-Acetamido-3'-nitrobimesityl.--The acetylation of 3-amino-3'-nitrobimesityl was carried out according to the procedure of Moyer and Adams (8) in 80 per cent yield. The compound melted at 176°-177°C.

Attempted Condensation of 3-Acetamido-3'-nitrobimesityl with Mesitylene.--A 100 ml. three-necked flask, equipped with a stirrer and a thermometer,

was placed in an ice-water mixture. To the flask was added a mixture of 1.5 g. of 3-acetamido-3'-nitrobimesityl, 15.0 ml. of glacial acetic acid, 5.0 ml. of acetic anhydride, 2.5 g. of anhydrous sodium acetate, and 1.5 g. of phosphorous pentoxide. When the temperature of the mixture dropped to 8°-10°C., a solution of 0.2 ml. (0.35 g.) of nitrosyl chloride in 1.0 ml. of acetic anhydride was added. The nitrosyl chloride caused the solution first to turn green, then gradually to turn brown. The solution was stirred for 45 minutes longer, then was poured into ice water. A white precipitate and an oily, gummy material separated from the solution. The entire reaction mixture was extracted with several portions of mesitylene totaling 100 ml. The mesitylene extract was dried over anhydrous sodium acetate for 18 hours. Mesitylene was then removed by fractionation until a volume of about 10 ml. remained. The white solid in the remaining mesitylene solution was filtered off. This solid had a melting point of 176°-177°C., that of the starting material. A mixed melting point was undepressed. Evaporation of the remaining mesitylene left a brown gum which resisted solidification and purification. Freezing, crystallization from 95 per cent ethanol, crystallization from benzene, as well as vacuum sublimation were all tried with no success.

Attempted Preparation of 2,2',2",4,4',4",6,6',6"-Nonamethyl-m-terphenyl

Preparation of Dinitromesitylene.--The method of Kuster and Stallberg (60) was used to prepare this material in 90 per cent yield. The melt-

(60) F. W. Kuster and A. Stallberg, Ann., 278, 207 (1894)

ing point of 85°-86°C. agreed with the 86°C. value reported by Kuster and Stallberg.

Preparation of Diaminomesitylene.--The method of Fittig (61), by which dinitromesitylene is reduced with tin and hydrochloric acid was used to prepare this compound. For the purification step, however, vacuum sublimation at 75°-85°C. and 1 mm. pressure was used. Diaminomesitylene, melting at 89°-90°C., was obtained in 78 per cent yield. Fittig reported a melting point of 90°C.

Preparation of Diacetamidomesitylene.--Diaminomesitylene was acetylated by acetic anhydride according to the method of Adams and Chase (34) in 40 per cent yield. However, the melting point reported by Adams and Chase was 320°-325°C., whereas the melting point here was 340°-345°C.

Attempted Condensation of Diacetamidomesitylene with Mesitylene.--A 100 ml. three-necked flask, equipped with a stirer and a thermometer, was set in a pan of ice and water. To the flask was added 1.1 g. of diacetamidomesitylene, 20.0 ml. of glacial acetic acid, 8.0 ml. of acetic anhydride, 2.0 g. of anhydrous sodium acetate, and 0.5 g. of phosphorous pentoxide. When the temperature dropped to 9.0°C., a mixture of 0.5 ml. (0.78 g.) of nitrosyl chloride in 1.0 ml. of acetic anhydride was added dropwise. The color of the solution assumed a greenish tinge. Stirring was continued for an hour. At the end of this time the temperature was 15.0°C. and the color of the solution had turned yellow. The contents of the flask were then poured into three times its volume of ice water. A white solid precipitated leaving a green

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(61) R. Fittig, Ann., 141, 129 (1867).

supernatant liquid. The solid was recovered by filtration and was washed with water. Its dry weight was 0.3 g. The white material melted at 340°-345°C., indicating that it was unreacted starting material.

The aqueous mixture was extracted with two cold 50 ml. portions of mesitylene, the extract dried over anhydrous sodium acetate, and then fractionated to a small volume. Evaporation of the remaining mesitylene left a small volume of oil which contained a small amount of white solid. A cold 95 per cent ethanol wash removed most of the oil and left the solid fairly clean. The solid, upon being recrystallized from 95 per cent ethanol, had a melting point of 165.0°-167.5°C. However, this solid seemed to be a mixture of close melting compounds and was never obtained pure enough for analysis. In order to obtain a single pure compound, crystallization from ethanol, vacuum sublimation, and chromatography on a silicic acid-chloroform column were all tried but without success.

Attempted Preparations of 2,2",4,4",6,6"-Hexamethyl-o-terphenyl

Attempted Condensation of 1,2-Diacetamidobenzene with Mesitylene.--A 500 ml. three-necked flask, equipped with a stirrer and a thermometer, was set in an ice bath. To the flask was added a mixture of 4.9 g. of 1,2-diacetamidobenzene, 8.0 g. of anhydrous sodium acetate, 85 ml. of glacial acetic acid, 20.0 ml. of acetic anhydride, and 1.0 g. of phosphorous pentoxide. When the temperature of the mixture reached 5°-10°C, 6.0 ml. of nitrosyl chloride in 20.0 ml. of cold acetic anhydride was added to the flask and with stirring. Stirring was continued for one

hour, during which time the temperature rose to 12°C. The contents of the flask was then poured into three times its volume of ice water. The cold mixture was extracted quickly with two 50 ml. portions of mesitylene. An irritating orange gas, probably unreacted nitrosyl chloride, evolved during the extraction. The mesitylene extract was then washed with water and dried over anhydrous sodium sulfate.

All but about five milliliters of the mesitylene was then removed by fractionation. A small amount of impure solid, which appeared to be a mixture, was found in the remaining mesitylene. The solid was filtered off and dissolved in hot 95 per cent ethanol. However, upon being cooled, a brown oil separated from the solution. Under vacuum sublimation at 40°-45°C. and 1 mm. pressure, the oil deposited a white solid on the condenser. This solid, suspected of being mostly o-phenylenediamine, melted poorly at 89°-92°C. A wash with water removed most of this solid, leaving behind a small amount of gummy oil which slowly solidified. The solid, only about enough for a melting point, melted poorly at 75°-80°C.

2,4,6-Trimethyl-2'-nitrobiphenyl.--This compound was the product from the first step of an alternate route to 2,2",4,4",6,6"-hexamethyl-o-terphenyl. Work on this route was discontinued after this step.

A 100 ml. three-necked flask, equipped with a stirrer and a thermometer, was set in an ice and water mixture. To the flask was added 2.0 g. of o-nitroacetanilide, 10.0 ml. of glacial acetic acid, 2.0 ml. of acetic anhydride, 1.5 g. of anhydrous sodium acetate, and 0.5 g. of phosphorous pentoxide. When the temperature of the mixture fell to 10°C., 0.6 ml. of nitrosyl chloride in 3.0 ml. of acetic anhydride was added dropwise to the solution with stirring. This addition

caused the solution to assume a green color which gradually faded to brown. The brown solution was stirred for 20 minutes longer, and then was poured into 50 ml. of ice water. An oil which separated was extracted as quickly as possible with 165 ml. of cold mesitylene in three portions. The mesitylene was quickly washed with water then dried over anhydrous sodium sulfate for 12 hours. Removal of the mesitylene by fractionation left a small amount of oil mixed with a yellow solid. The solid was removed by filtration through a coarse sintered glass funnel. The solid (0.7 g.), recrystallized from 95 per cent ethanol, melted at 93°-94°C. which indicated it to be unreacted o-nitroacetanilide. A mixed melting point with o-nitroacetanilide was undepressed.

The oil from the filtration was steam distilled, and from the distillate was recovered a clean orange oil which solidified upon cooling. After recrystallization from 95 per cent ethanol, the yellow solid melted at 64°-65°C.

Anal. calc. for $C_{16}H_{12}N_2O_5$: N, 5.80

Found: N, 5.57

Attempts to Prepare o-Terphenyls with Hindered Rotation Utilizing the Diels-Alder Reaction

Attempted Preparation of 2,2",4,4",6,6"-Hexamethyl-o-terphenyl-4',5'-dicarboxylic Acid

Preparation of Acetomesitylene.--This compound was prepared by the general Friedel-Crafts method for ketone preparation using acid anhydrides (62).

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(62). C. R. Noller and R. Adams, J. Am. Chem. Soc., 46, 1889 (1924).

The crude product obtained was fractionated under reduced pressure through a silver-jacketed column, 27 cm. in length and 2 cm. in diameter, packed with 1/8 inch glass helices. The bulk of the acetomesitylene distilled at 100°C. under 4.25 mm. pressure. A 74 per cent yield was realized from the reaction. On several occasions the fractionated product was slightly yellow in color. It was found that the yellow color could be removed by extracting an ethereal solution of the acetomesitylene with a 20 per cent sodium hydroxide solution until the extracting base solution was only slightly colored. The ether solution was then washed well with 1:2 hydrochloric acid, once with water, then dried over calcium chloride. Vacuum distillation from a Claisen flask then yielded a water-clear product.

The Bimolecular Reduction of Acetomesitylene.--

Attempted Photochemical Reduction.--This attempt was patterned after the procedure of Bachmann (63). Ultraviolet radiation was used, however, rather than sunlight.

A solution of 10.0 g. of acetomesitylene, 175 ml. of isopropyl alcohol and one drop of glacial acetic acid was placed in a quartz radiation cell. The solution was irradiated by a mercury vapor ultraviolet lamp for eight hours. The solvent was evaporated and the residual oil was steam distilled from a dilute hydrochloric acid solution to remove unreacted acetomesitylene. A 7.1 g. recovery of acetomesitylene was obtained. The residue from the steam distillation was 1.8 g.

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(63) W. E. Bachmann, Organic Syntheses, Coll. Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1957, p. 71.

of a dark brown oil which soon solidified. This solid was taken up in a few ml. of chloroform and run through a silicic acid-chloroform chromatographic column. While the solid was separated into three distinct bands, evaporation of each chloroform fraction yielded a brown glassy solid. None of the desired pinacol could be isolated from any fraction.

Attempted Electrolytic Reduction.--The equipment used and the procedure followed was essentially that described by Swann and coworkers (64).

A mixture of 5.0 g. of acetomesitylene and 50.0 ml. of catholyte was placed in an unglazed porcelain cup used as the cathode cell. The catholyte was a solution of 20.0 g. of potassium acetate dissolved in 15.0 ml. of distilled water and 35.0 ml. of ethanol. The anolyte was a 40 per cent potassium carbonate solution. The cathode used was a small sheet of tin leaf which was anodized in dilute sulfuric acid before use. The reaction was run for five hours at 85°-90°C. with a current density of 0.005 amp./cm^2. At the end of this time, the reaction mixture was poured into water. The mixture formed was made slightly acid with hydrochloric acid and steam distilled to remove unreacted acetomesitylene and any methyl mesityl carbinol that might have been formed. The aqueous mixture left from the steam distillation was extracted with ether. The solid left upon evaporation of the ether was crystallized once from 95 per cent ethanol. The best yield obtained

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(64) S. Swann, Jr., P. E. Ambrose, R. C. Dale, R. C. Rowe, H. M. Ward, H. D. Kerfman, and S. Axelrod, Trans. Electrochem. Soc., 85, 231 (1944).

was 0.6 g. (12.0 per cent of the theoretical) of material of questionable purity, melting poorly at 145°-150°C.

Reduction by Aluminum Amalgam.--The procedure used for this preparation was essentially that which Sisido and Nozaki (35) used for the reduction of acetophenone.

In a 1000 ml. round-bottomed flask was placed a solution of 38.7 g. of acetomesitylene in 200 ml. of anhydrous, thiophene-free benzene and 300 ml. of absolute ethanol. Then 17.0 g. of eight mesh or finer granular aluminum and 0.5 g. of mercuric chloride was added and a reflux condenser was set in place. Within a minute bubbles were seen rising from the aluminum. The flask was then set on a steam bath and the mixture was refluxed for 40 hours. After about six or seven hours a gray, jelly-like mass that formed became so thick that it prevented the natural agitation caused by the bubbling and refluxing solvent. Enough ethanol-benzene solvent, in the proportion stated above, was added to allow agitation and circulation throughout the flask. At the end of the 40 hours, the reaction product was decomposed by pouring it on a mixture of 200 g. of ice and 30 ml. of concentrated hydrochloric acid. The aqueous layer was separated and discarded. The benzene layer was washed several times with 1:2 hydrochloric acid, then several times with water. The benzene was evaporated and the remaining oil was steam distilled. Unreacted acetomesitylene and methyl mesityl carbinol steam distilled, leaving a white solid in the flask. The methyl mesityl carbinol that steam distilled solidified slowly in the distillate and was removed by filtration. The filtered oily distillate was then ether extracted. After the ether was evaporated, 18.5 g. of unreacted aceto-

mesitylene remained. In the distillation flask remained 13.2 g. of white solid which was filtered off and dried.

A partial separation of the products in this white solid was achieved by first digesting the 13.2 g. of product in enough chloroform at room temperature to leave a little of the material undissolved. The chloroform was then heated slightly until all of the material dissolved. The warm solution was set aside and allowed to cool. The crystals that slowly formed were filtered off and washed with cold chloroform. After several crystallizations from 95 per cent ethanol the large, clear crystals melted at 172.5°-173.5°C.

The rest of the material in the chloroform solution was chromatographed on a silicic acid-chloroform column. Only one broad white band developed. However, by carefully collecting fractions as described, five products were isolated. The column used was a tube 4.3 cm. in diameter and equipped with a permanent coarse sintered glass column support. The column was packed with 177 g. of silicic acid slurried in chloroform, which gave a packed height of 21.0 cm. The product, in 20.0 ml. of chloroform, was put on the top of the column and eluted with chloroform. The relative positions of the fractions taken from the column are shown in Figure 20.

Fraction #1 was the material in the first half of the heavy white band. Evaporation of the collected chloroform and crystallization of the residue twice from 95 per cent ethanol yielded white needles melting at 92.0°-93.0°C.

Fraction #2 was the material taken from after fraction #1 until the end of the "tailing". Evaporation of the chloroform and crystal-

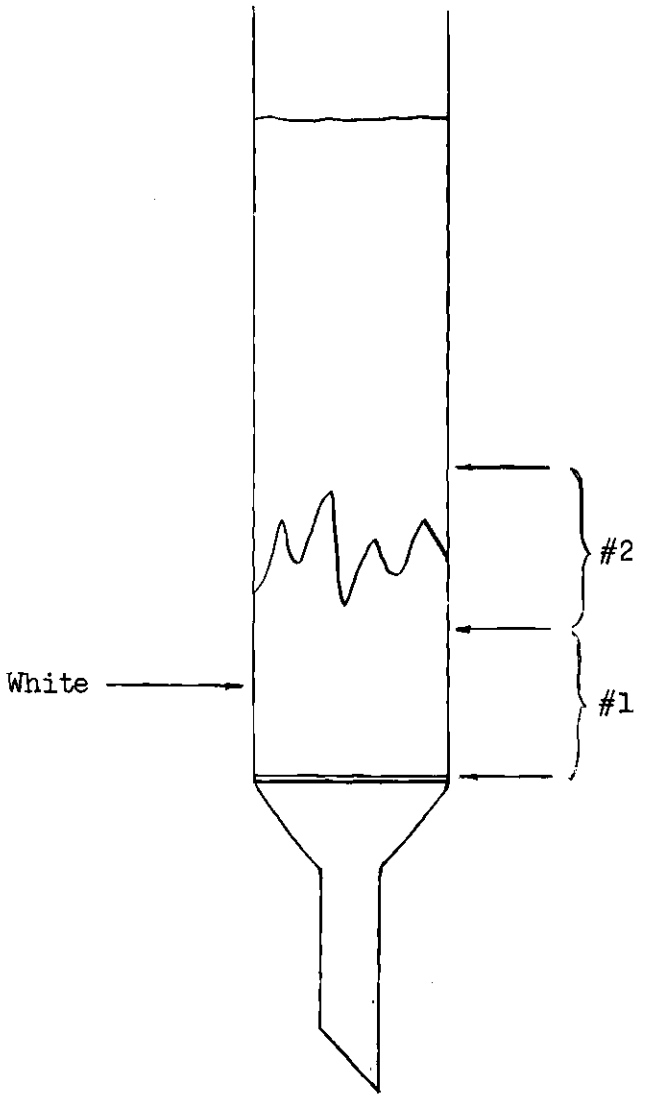

Figure 20. Chromatogram of the Products from the Aluminum Amalgam Reduction of Acetomesitylene.

lization of the residue several times from 95 per cent ethanol yielded white crystals which melted at 119.5°-120.5°C.

Fractions #1 and #2 were the only fractions that could be taken by sight. A series of 10 ml. fractions were then taken. Several fractions following fraction #2 yielded only a few drops of oil and no solid. The fractions collected thereafter began to contain white solid, the amounts of which increased to a maximum and then decreased to practically none. The weight of white solid per 10 ml. fraction is plotted in Figure 21. The melting point of the solids recovered from all of these fractions was about 171°-173.5°C. After the fractions were combined and crystallized from 95 per cent ethanol, the obtained crystals melted at 172.5°-173.5°C.

The column was now "stripped" by eluting with a 1:1 chloroform-methanol mixture. The residue from the complete elution of the column was a white solid contaminated with a small amount of oil. About ten ml. of 95 per cent ethanol was added to it and stirred for about a minute at room temperature. The solid resisting solution was filtered off and recrystallized from 95 per cent ethanol several times until a melting point of 155°-156°C. was obtained.

The material which dissolved in the ethanol at room temperature was much too soluble to be recrystallized from 95 per cent ethanol, and from an ethanol-water mixture it precipitated as an oil. So the ethanol was evaporated and the material was taken up in ligroin. The recrystallizing flask was set in dry ice for about half an hour. By this time a fine white solid had precipitated. The solid was then quickly filtered off. One more similar crystallization yielded a white solid which

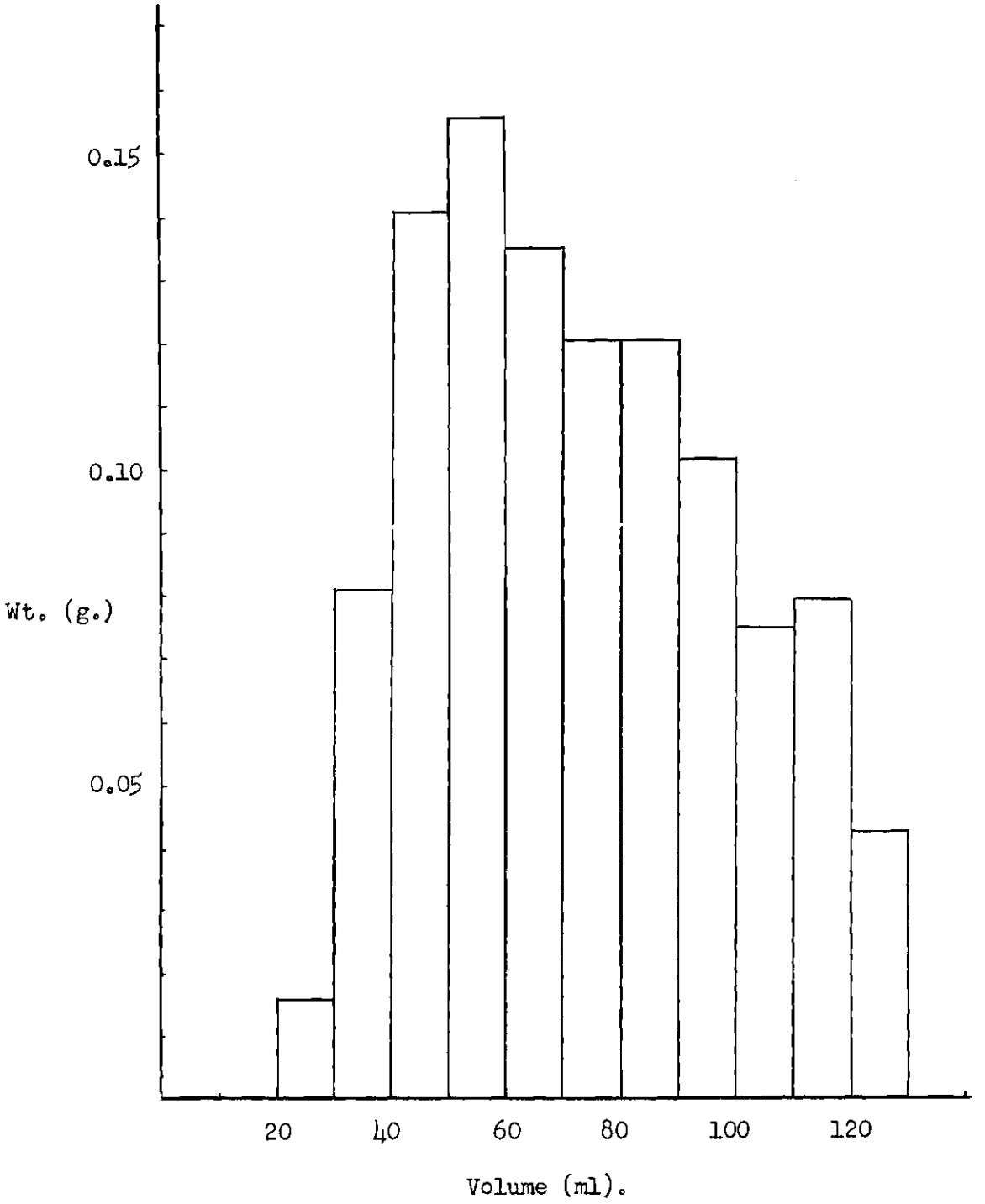

Figure 21. Chromatographic Isolation of One Compound (m.p. 172.5°-173.5°C) Obtained from the Reduction of Acetomesitylene. Weight of Solid per Ten Ml. Fraction of Chloroform.

melted at 70°-71°C.

The five reaction products were identified as follows:

meso-2,3-Dimesityl-2,3-butanediol.--The large clear crystals of this compound melted at 172.5°-173.5°C. The infrared spectrum (Figure 31) of these crystals contained absorption bands which were unmistakeably those of the hydroxyl group, and in every way was in harmony with the expected spectrum of the proposed compound.

Anal. calc. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26

Found: C, 80.98; H, 9.25

These crystals were cleaved to acetomesitylene when reacted with periodic acid in the following manner. In a 100 ml. Erlenmeyer flask was placed a mixture of 1.0 g. of the crystals, 5.6 ml. of a 0.54 molar aqueous periodic acid solution, and 30 ml. of a 1:1 ethanol-ethyl acetate solution. The flask was warmed on a water bath at 50°-60°C. for about two hours, with frequent shaking. The mixture was then cooled and neutralized with a saturated barium hydroxide solution. A yellow oil slowly formed on the surface of the mixture. The oil was separated in a separatory funnel and dried in an ether solution over calcium sulfate. The ether was then evaporated and the refractive index of the residual oil was checked with that of acetomesitylene.

Acetomesitylene, $n_D^{20} = 1.5175$ (62)

Oil, $n_D^{26} = 1.5168$

An unsuccessful attempt was made to prepare the diacetate ester of this diol by treating it with acetyl chloride and dimethylaniline (65).

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(65) C. R. Hauser, B. E. Hudson, B. Abramovitch, and J. C. Shivers, Organic Syntheses, Coll. Vol. III, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 142.

The behavior of this diol upon being heated just above its melting point was similar to that reported for benzopinacol (39). A small test tube was half immersed in an oil bath held at 180°C. To the test tube was added 0.5 g. of meso-2,3-dimesityl-butanediol. The bath temperature was kept at about 180°C. for three hours and then allowed to cool. The white solid had become a yellow oil. The oil was micro distilled in a vacuum sublimation apparatus at 70°-90°C. and 1 mm. pressure. A colorless oil was collected in a small glass bucket which was hung below the condenser. A small amount of white solid sublimed along with the distillation and deposited on the condenser. The refractive index of the oil was checked with that of acetomesitylene.

Acetomesitylene, $n_D^{20} = 1.5175$ (62)

Oil, $n_D^{26} = 1.5181$

An attempt was made to resolve this glycol, as well as the suspected dl isomer, by crystallization. The technique was the same as that used for the dl glycol, and is described below.

dl-2,3-Dimesityl-2,3-butanediol.--The infrared spectrum (Figure 32) of this compound was that of a typical alcohol. The melting point of this compound, if taken slowly, was 144.5°-145.5°C. If the melting point was taken rapidly it melted at 155°-156°C.

Anal. calc. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26

Found: C, 81.33; H, 9.16

This compound was cleaved to acetomesitylene with periodic acid by the same procedure used for the meso isomer, described above.

An attempt was made to resolve this glycol by crystallization (40). Dilute solutions in ether, ethanol, ethyl acetate, and chloroform

were made by dissolving 0.5 g. samples of the glycol in 200-300 ml. of solvent. These solutions were set aside and allowed to evaporate slowly. The crystals thereby obtained were singly examined for optical activity but none showed any noticeable rotation.

trans-2,3-Dimesityl-2,3-epoxybutane.--The white needles of this compound melted at 92°-93°C. The Baeyer test for unsaturation performed on these needles at room temperature proved negative. The compound also failed to discharge significantly the color of a solution of bromine in carbon tetrachloride. An iodoform test was negative as was an attempt to form the oxime with hydroxylamine and pyridine.

Anal. calc. for $C_{22}H_{28}O$: C, 85.66; H, 9.15

Found: C, 85.04; H, 9.67

Mol. Wt. calc. for $C_{22}H_{28}O$: 308

Found: 279 (Rast)

An attempt was made to identify this material more decisively by hydrolyzing the oxide ring to form one of the 2,3-dimesityl-2,3-butanediol isomers. A mixture of 0.1 g. of this compound, 15 ml. of water and 0.5 ml. of perchloric acid was refluxed for six hours. The melting point of the recovered material mixed with pure starting material was 89°-91°C.

The conversion of this oxide to its diacetate ester derivative was tried several ways.

A mixture of 0.35 g. of the oxide, 3.0 ml. of acetic anhydride, and 0.5 ml. of pyridine was refluxed for three hours. In less than a half hour the mixture had turned brown. At the end of the three hours the reaction was cooled and water was added to destroy the excess

acetic anhydride. The solid was filtered off, washed with water and dried. After crystallization from ethanol the solid melted at 90°-91°C. This material mixed with pure starting material melted at 89°-91°C.

Two more attempts were made to obtain the diacetate by using sulfuric acid as catalyst with acetic anhydride. One trial was run in a sealed tube and the other was run in an open flask. Upon being warmed, the reaction in both trials charred badly.

cis-2,3-Dimesityl-2,3-epoxybutane.--The clear flakes of this material melted at 119.5°-120.5°C. The Baeyer test for unsaturation performed on these flakes at room temperature proved negative. The compound discharged the color of bromine in carbon tetrachloride only very slowly. An iodoform test was negative, as was an attempt to form the oxime of the compound with hydroxylamine and pyridine. The infrared spectrum of this compound (Figure 27) was very similar to that of trans-2,3-dimesityl-2,3-epoxybutane (Figure 28).

Anal. calc. for $C_{22}H_{28}O$: C, 85.66; H, 9.15

Found: C, 85.31; H, 9.14

Mol. Wt. calc. for $C_{22}H_{28}O$: 308

Found: 268 (Rast)

Methyl Mesityl Carbinol.--The 70°-71°C. melting point of this material is identical with the literature value for methyl mesityl carbinol (66).

Anal. calc. for $C_{11}H_{16}O$: C, 80.43; H, 9.82

Found: C, 80.44; H, 9.90

This aluminum amalgam reduction of acetomesitylene was run several

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(66) A. Klages and P. Allendorf, Ber., 31, 998 (1898).

times. The above compounds were found in the product mixture in the following approximate percentages.

meso-2,3-dimesityl-2,3-butanediol	35 per cent
dl-2,3-dimesityl-2,3-butanediol	14 per cent
trans-2,3-dimesityl-2,3-epoxybutane	32 per cent
cis-2,3-dimesityl-2,3-epoxybutane	12 per cent
methyl mesityl carbinol	7 per cent

2,3-Dimesityl-1,3-butadiene.--

From the Dehydration of meso-2,3-Dimesityl-2,3-butanediol.--An intimate mixture of 1.0 g. of meso-2,3-dimesityl-2,3-butanediol and 1.0 g. of freshly fused potassium bisulfate was placed in a 25 ml. vacuum distilling flask. The distilling flask was of a design suitable for the vacuum distillation of solids. The flask was immersed up to its side arm in an oil bath. The temperature of the bath was raised to 125°C. while a pressure of 0.5 mm. was maintained by a vacuum pump. At the end of two hours of operation a white solid had deposited on the upper wall of the flask and on the side arm. The apparatus was dismantled and the white material was scraped from the side arm and the upper part of the flask. After washing the solid with water and crystallizing it from methanol, it was recrystallized from ethyl acetate, using just enough ethanol to bring about incipient cloudiness. The final crystallization yielded 0.3 g. of clear crystals. Their melting point was 187°-188°C.

The crystals did not discharge the color of bromine in carbon tetrachloride.

Anal. calc. for $C_{22}H_{26}$: C, 90.97; H, 9.02

Found: C, 91.09; H, 9.01

An attempted dehydration of meso-2,3-dimesityl-2,3-butanediol by treatment with acetyl bromide failed (67).

A mixture of 1.0 g. of meso-2,3-dimesityl-2,3-butanediol and a pinch of hydroquinone was placed in a 25 ml. Erlenmeyer flask. To this mixture was slowly added 2.5 ml. of acetyl bromide. A brisk reaction took place with frothing and evolution of heat. The large crystals of the diol disappeared and a fine white powder separated from the solution. After allowing the flask to sit for about an hour, the excess acetyl bromide was removed by reduced pressure distillation. The residual solid was then cautiously neutralized with sodium bicarbonate, filtered, and washed with water. The solid was crystallized many times from 95 per cent ethanol, but no pure product was obtained. A separation by chromatography on a silicic acid-chloroform column was attempted. However, the product still resisted purification.

From 2,3-Dimesityl-2,3-epoxybutane.--A mixture of 70 ml. of glacial acetic acid and 5.0 g. of 2,3-dimesityl-2,3-epoxybutane isomers was refluxed in a 200 ml. flask for three and one-half hours. The mixture was then poured into about an equal volume of water and allowed to stand over night. At the end of this time, a layer of oil had formed at the top of the mixture and at the oil-water interface a small amount of rock-like crystals had formed. The crystals were removed by filtration and washed with a cold 1:1 ethanol-water mixture. After

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(67) C. F. H. Allen, C. G. Eliot, and A. Bell, Can. J. Research, 17B, 75 (1939).

being recrystallized from ethyl acetate and ethanol, the crystals weighed 0.8 g. and melted at 187°-188°C.

Anal. calc. for $C_{22}H_{26}$: C, 90.97; H, 9.02

Found: C, 91.22; H, 8.82

3,3-Dimesitylbutanone-2.--meso-2,3-Dimesityl-2,3-butanediol was dehydrated by potassium bisulfate and 2,3-dimesityl-1,3-butadiene was isolated from the reaction mixture as described above.

The material remaining in the bottom of the flask was washed with water to remove the inorganic salt. The remaining mixture was then fractionally crystallized from methanol. The first fraction to precipitate was 0.43 g. of unreacted meso-2,3-dimesityl-2,3-butanediol. The methanol was then evaporated to about one third its volume, whereupon 0.2 g. of a more soluble fraction precipitated. The crystals of this fraction melted at 95°-97°C. Repeated recrystallization from ethanol and water raised the melting point to 97.5°-98.5°C.

Anal. calc. for $C_{22}H_{28}O$: C, 85.66; H, 9.15

Found: C, 85.49; H, 9.09

This material refluxed for three hours with hydroxylamine hydrochloride and pyridine in absolute ethanol failed to give an oxime. An iodoform test performed on this compound failed to yield any iodoform, but yellow crystals did form. These crystals, after recrystallization from 95 per cent ethanol, melted at 133°-136°C. A halogen test on a sodium fusion of the yellow crystals was positive. After standing exposed to the light for several weeks, the crystals became dark purple.

Attempted Preparation of 3',4',5',6'-Tetrahydro-2,2",4,4",6,6"-hexamethyl-o-terphenyl-4',5'-dicarboxylic Acid

Attempted Addition of 2,3-Dimesityl-1,3-butadiene to Maleic Anhydride.--A solution of 0.25 g. of 2,3-dimesityl-1,3-butadiene and 0.3 g. of maleic anhydride in 20.0 ml. of benzene was placed in a 100 ml. flask. The solution was refluxed for two hours. At the end of this time the benzene was poured into an evaporating dish. Evaporation of the benzene left an oil which solidified quickly upon being rubbed. The solid was washed well with water. It was then recrystallized from ethyl acetate using just enough 95 per cent ethanol to bring about incipient cloudiness. A single well-formed crystal weighing 0.1 g. slowly crystallized. Its melting point was 186°-188°C., indicating unreacted starting material. A mixed melting point with 2,3-dimesityl-1,3-butadiene was undepressed.

CHAPTER IV

CONCLUSIONS

All the synthesis routes attempted in this research involved molecules containing reaction sites flanked by bulky groups and were hence subject to the poor yields expected from the ortho, or proximity, effect.

The use of dimethylformamide as a diluent in certain Ullmann reactions seems to cause a slight decrease in the yield of product.

Reduction of dimethyl 6,6'-dinitrodiphenate can give rise to 5,10-dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene and 1,10-dicarbmethoxybenzo(c)cinnoline-5-oxide (both heretofore unreported), as well as the previously reported dilactam of 6,6'-diaminodiphenic acid.

Reactions which involve the 2 and 2' biphenyl positions often yield products peculiar to this system, such as the cyclic dilactam, the cyclic dihydroxamic acid, the cyclic azoxy compound, and the iodonium iodide observed in this work.

A convenient preparation of 2,4-diacetamidotoluene and 2,6-diacetamidotoluene from o-nitrotoluene has been developed in this research.

The aluminum amalgam bimolecular reduction of acetomesitylene yields five products in contrast to the one product, a pinacol, reported from the analogous reduction of acetophenone.

Bulky substituents in the 2 and 3 positions of 1,3-butadiene, such as the mesityl group tend to prevent the addition of the butadiene to maleic anhydride.

CHAPTER V

RECOMMENDATIONS

Most of the terphenyls on which syntheses were attempted in this research were substituted with groups such as CH_3, NO_2, and $COOCH_3$, that represent the extreme in steric hindrance. A Hirschfelder model of o-terphenyl reveals that only a relatively small group need be substituted in the ortho positions of the terminal rings to prevent free rotation. Indeed, a methyl group in just one ortho position on both terminal rings affords a definite hindrance. It is therefore recommended that at least one attempt be made by each of the three methods covered in this work to synthesize less heavily substituted o- and m-terphenyls.

In this research one attempt was made at a two step preparation of 2,4- and 2,6-diacetamidotoluene. First, o-nitrotoluene was nitrated. The resulting mixture of 2,4- and 2,6-dinitrotoluenes was catalytically hydrogenated over platinum oxide catalyst in the presence of acetic anhydride. The expected mixture of 2,4- and 2,6-diacetamidotoluenes could have been easily separated by a 1:1 acetic acid wash. However, the single hydrogenation tried in this work resulted in an intractable oil. If this synthesis could be accomplished it would save both time and labor in preparing these compounds. It is therefore suggested that this experiment be repeated with some adjusting of variables and with special regard for purity of materials.

Several compounds resulting from the iodination of m-nitroaniline with iodine monochloride have not been characterized. The iodine analysis obtained for each compound did not fit a simple mono-, di-, or triiodo-m-nitroaniline. Since these compounds seem to be unusual, their identity should be established by complete analysis and such chemical and physical tests as are needed.

The identity and steric configurations of the two 2,3-dimesityl-2,3-butanediol and 2,3-dimesityl-2,3-epoxybutane isomers obtained in the present work should be unambiguously determined. First, resolution of the diols should be attempted to establish the identity of the dl diol. l-Menthoxyacetic acid is suggested as the resolving agent. Conditions should then be sought to hydrolyze the rings of the 2,3-dimesityl-2,3-epoxybutanes to the corresponding diols. From the identity of the diols so obtained and from the fact that inversion takes place in the transformation, the identity of all four compounds could be determined.

The one attempt in the present work to add 2,3-dimesityl-1,3-butadiene to maleic anhydride failed. However, the addition should be tried under other conditions. This could include a sealed tube reaction at a higher temperature. Various workers have obtained fully aromatized Diels-Alder adducts by using nitrobenzene as the solvent as well as by using chloromaleic anhydride as the dienophile. Both of these techniques are promising for the present case in which a higher than ordinary temperature is suggested. Reversal of the addition reaction frequently occurs at elevated temperatures but aromatization of the adduct would prevent such reversal. An attempted addition under

ultraviolet light is also suggested. The results of some published and unpublished work in which this technique was used indicate that certain Diels-Alder reactions which fail under "ordinary" conditions do take place under the effect of ultraviolet light.

APPENDIX

INFRARED SPECTRA

Preparation of the Infrared Spectra

All the infrared spectra except that of dl-2,3-dimesityl-2,3-butanediol were recorded on a Perkin-Elmer Model 21 Spectrophotometer. The spectrum of dl-2,3-dimesityl-2,3-butanediol was recorded on a Beckman Infracord.

The spectra were made by the potassium bromide disc technique. The potassium bromide used was well dried and finely pulverized (325 mesh screen). The discs were prepared by intimately mixing and grinding 0.001 g. of the sample with 0.1 g. of potassium bromide in an agate mortar. The mixture was pressed into a one-half inch diameter disc by applying 35,000 pounds per square inch pressure upon it in a briqueting press. The pellets were placed in an adapter on the spectrophotometer. Most of the pellets made were translucent. However, adequate spectra were obtained by reducing the intensity of the reference beam of the spectrophotometer. This was done by inserting wire screens of suitable mesh into the path of the beam.

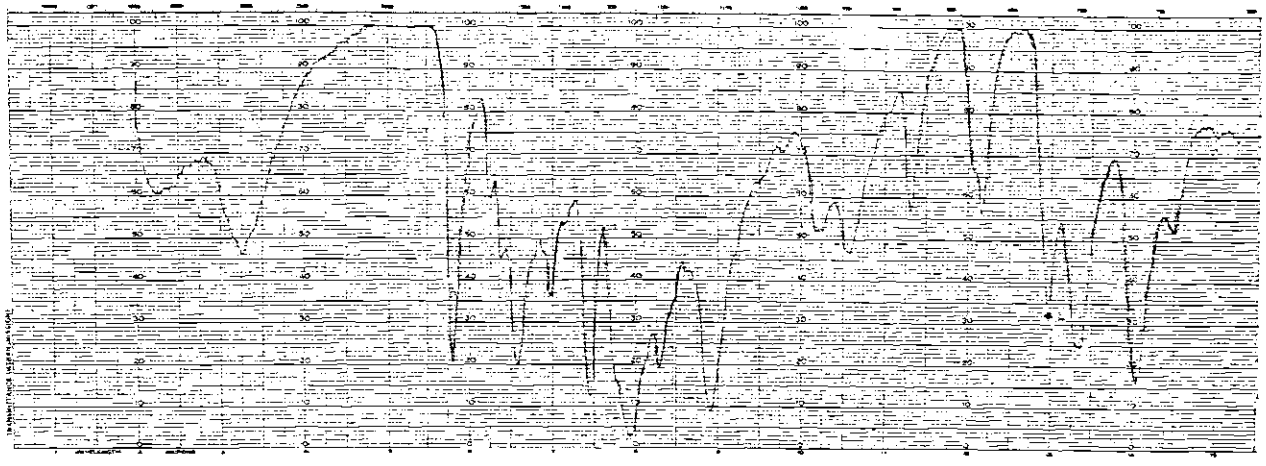

Figure 22. Dimethyl 6,6'-Dinitrodiphenate.

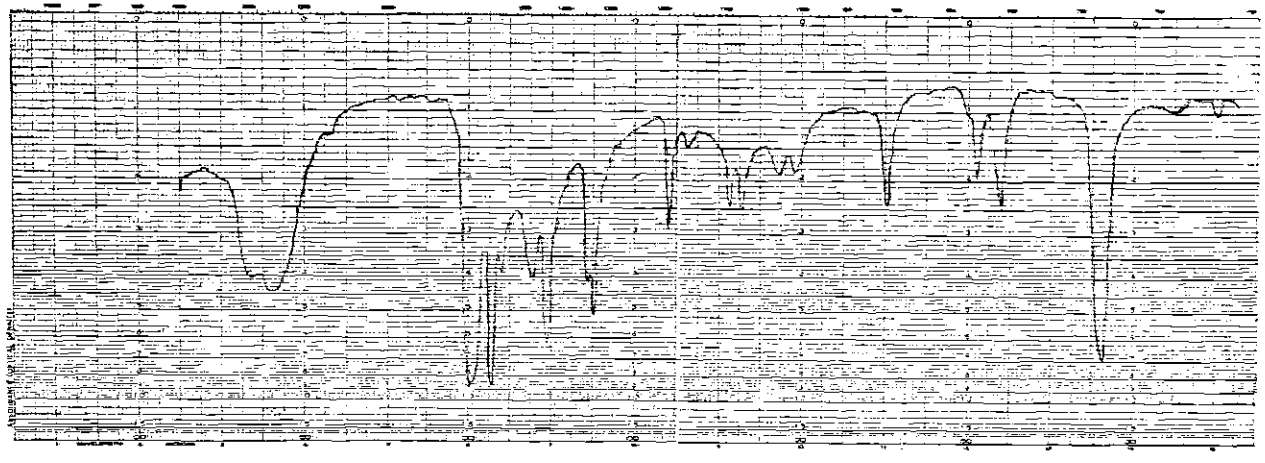

Figure 23. 5,10-Dioxo-4,5,9,10-tetrahydro-4,9-dihydroxy-4,9-diazapyrene.

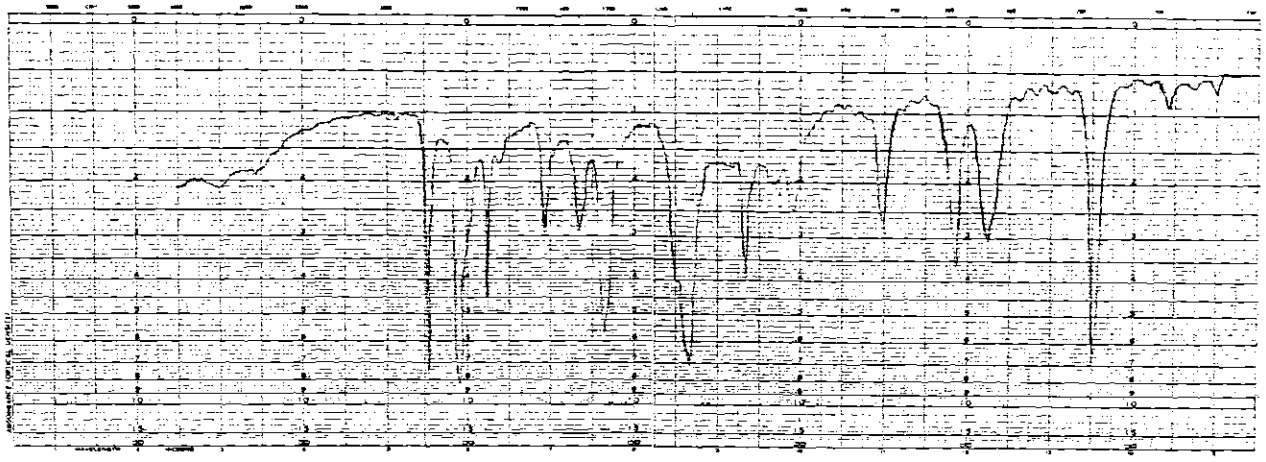

Figure 24. 5,10-Dioxo-4,5,9,10-tetrahydro-4,9-diacetoxy-4,9-diazapyrene.

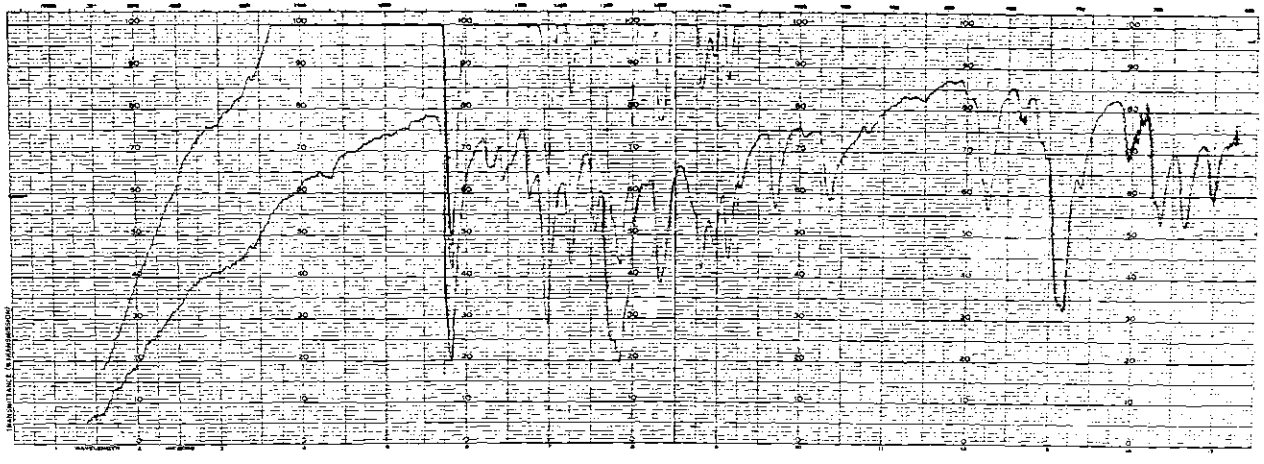

Figure 25. 1,10-Dicarbomethoxybenzo(c)cinnoline-5-oxide.

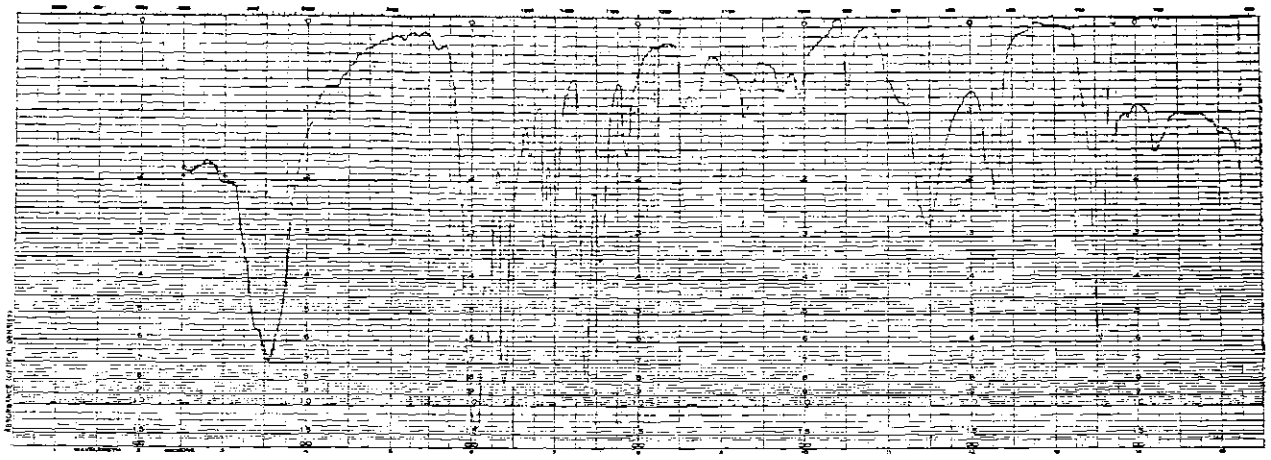

Figure 26. 6,6'-Diaminodiphenic Acid Dilactam.

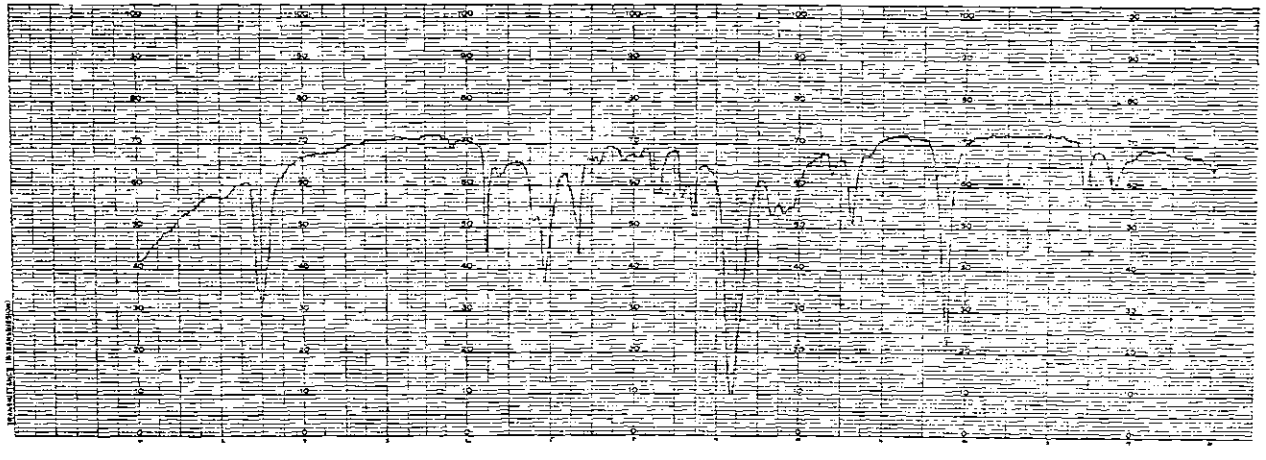

Figure 27. cis-2,3-Dimesityl-2,3-epoxybutane.

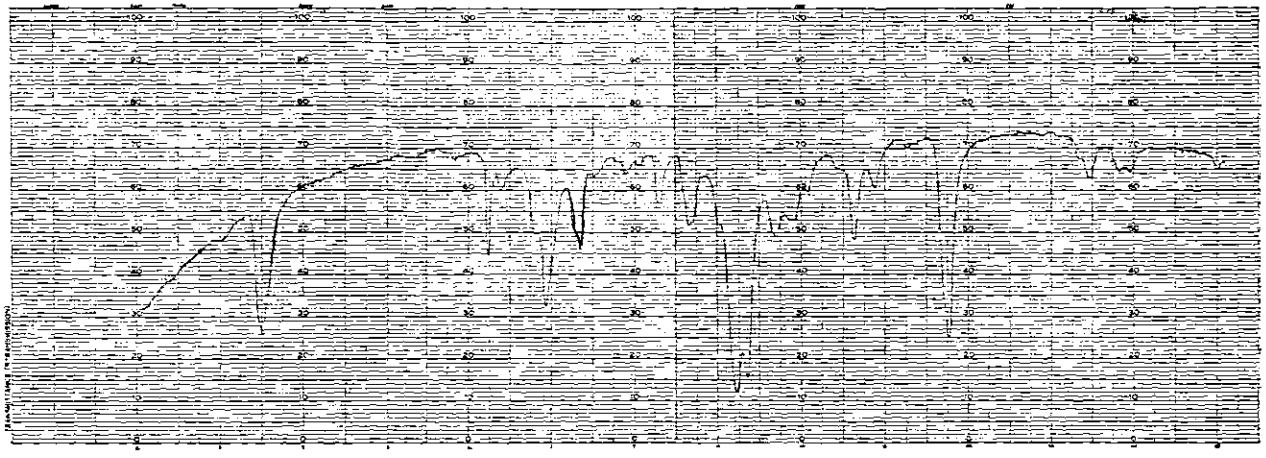

Figure 28. trans-2,3-Dimesityl-2,3-epoxybutane.

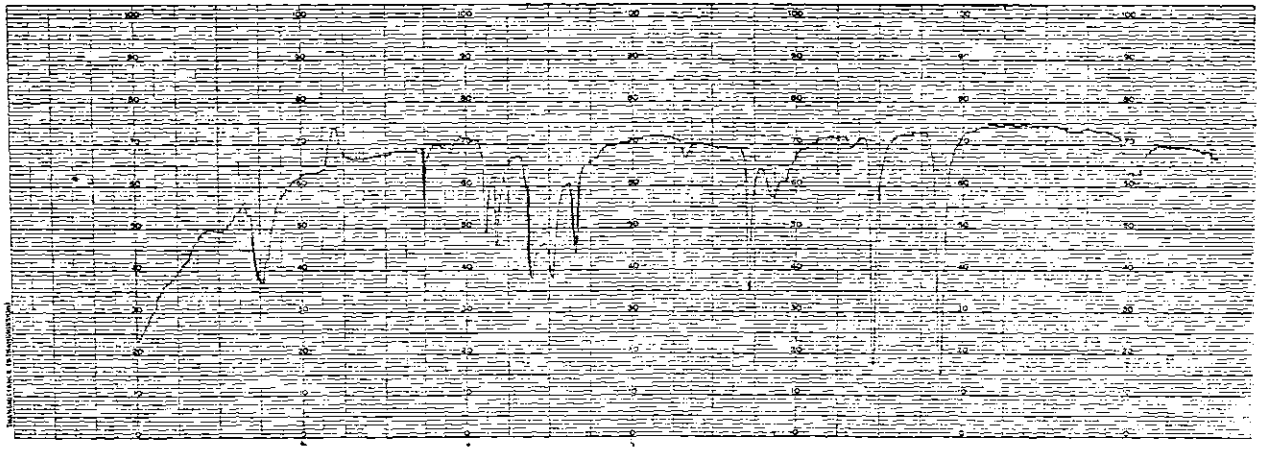

Figure 29. 2,3-Dimesityl-1,3-butadiene.

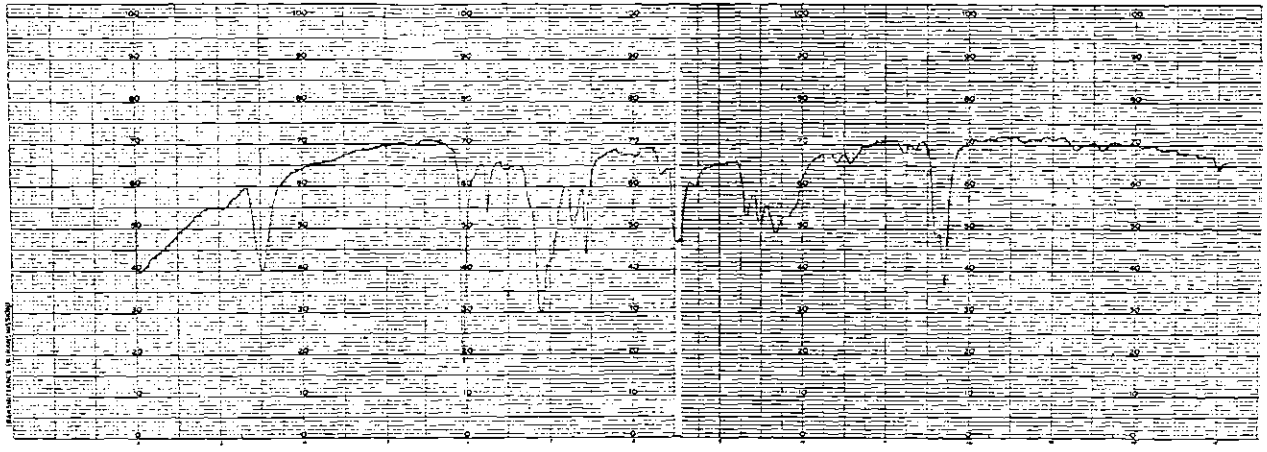

Figure 30. 3,3-Dimesitylbutanone-2.

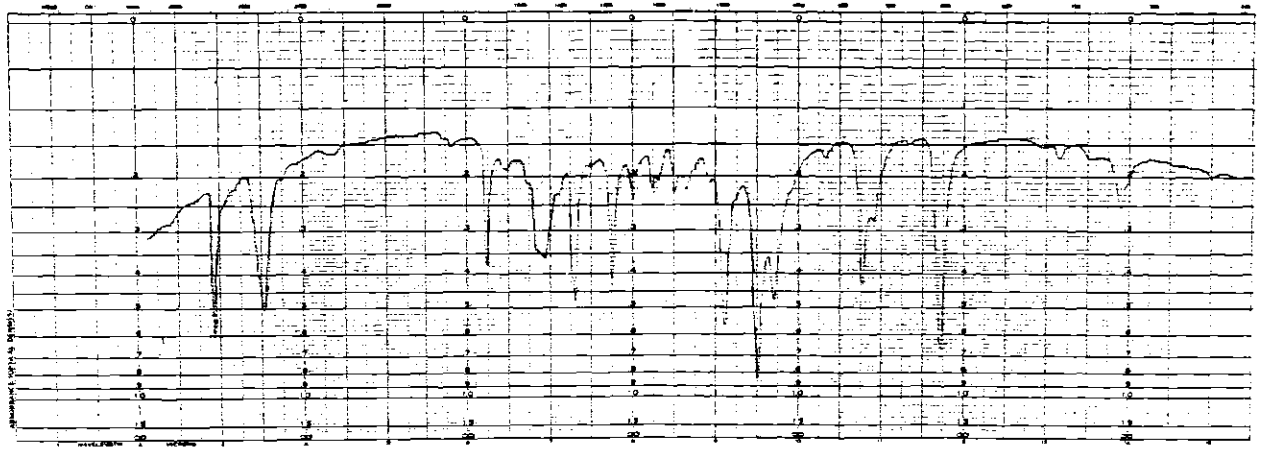

Figure 31. meso-2,3-Dimesityl-2,3-butanediol.

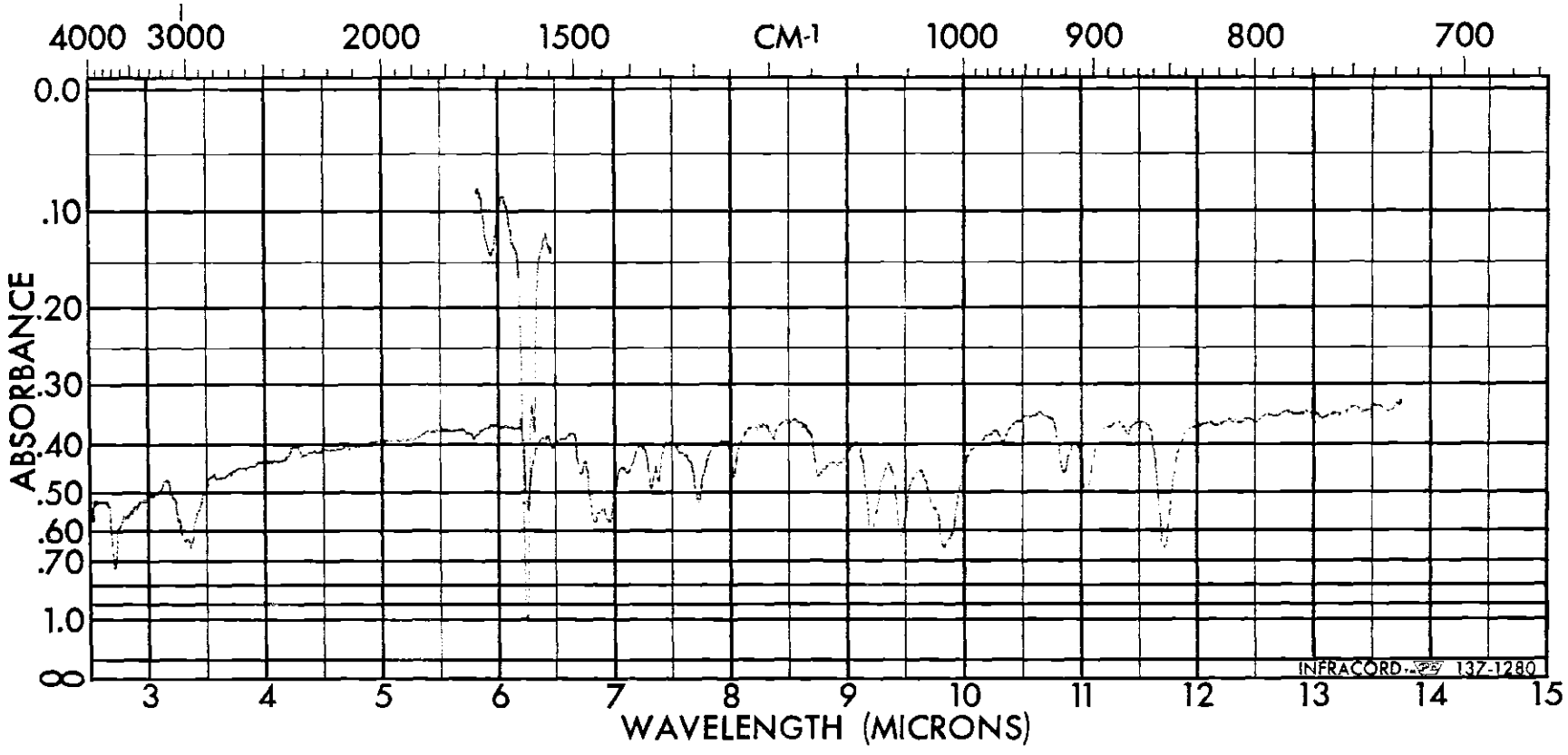

Figure 32. dl-2,3-Dimesityl-2,3-butanediol.

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VITA

Merrill Neilson O'Brien, Jr. was born in Camden, New Jersey, the son of Merrill and Jeanette O'Brien. He attended the public schools in Camden, and upon graduation from Camden High School worked several years as a printer. During World War II he served in the Merchant Marine and the Marine Corps. After the war he obtained the degree of Bachelor of Science in Chemistry from the University of Pennsylvania. For two years he then worked as Plant Chemist for James Lees and Sons, Co., Bridgeport, Pennsylvania. He left this position to enter Georgia Tech in order to work toward the degree of Doctor of Philosophy in organic chemistry. While at Georgia Tech he married the former Miss Ruth Bussard of Camden, New Jersey. In 1958 he accepted a position with the Celanese Corporation of America at Summit, New Jersey.